RESEARCH REPORT

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HYDROGEOCHEMICAL INVESTIGATION OF REACTIVE TAILINGS AT WAITE AMULET TAILINGS SITE, NORANDA QUEBEC - PHASE 3 - 1987 PROGRAM
VOLUME I - REPORT

Final Report by
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SUMMARY

The Reactive Acid Tailings/Wasterock Stabilization (RATS) Program is jointly funded by CANMET, the provinces and the mining industry. It has the objective of developing an inventory of practical techniques to achieve sufficient reduction in the impact of acid-generating tailings and wasterock to permit ultimate abandonment without on-going treatment or maintenance.

The Waite Amulet project within this program is a multi-year study with the overall objective of developing a better understanding of the hydrogeochemical processes and changes which occur in an acid-generating tailings area, as the basis for identifying and developing improved tailings management methods. Phase 1 (1985) included a preliminary site reconnaissance and drilling program. Phase 2 (1986) completed the definition of the site hydrogeology, evaluated the geochemistry of the unsaturated zone, and identified oxidation control options for 1987 field evaluation; equipment for monitoring precipitation, surface water and seepage was also purchased.

The 1987 field work (Phase 3) had four objectives: i) install the facilities required to develop water budgets and metal loadings; ii) relate mineralogy to the unsaturated zone porewater chemistry; iii) evaluate oxygen diffusion into the tailings; iv) monitor pore water movement and site geochemistry.

The following work was accomplished: i) the water monitoring facilities were installed, checked out and a limited amount of data collected; ii) an evaluation of mineralogy changes by J. Jambor of CANMET and the related assessment of unsaturated zone water chemistry by D. Blowes of University of Waterloo are in progress and will be incorporated into a supplementary report in late 1988; iii) oxygen profiles were established in sections of the tailings that were vegetated, bare and clay covered; iv) hydraulic conductivities have been established, the water table was monitored and extensive pore water analyses obtained.

The key recommendations for further work are to: i) establish water budgets and metal loadings over the next several years; and ii) focus the hydrogeological work on the seepage face and on modelling.

SOMMAIRE

Le programme de stabilization des résidus miniers et de la roche stérile (SRM-RS) est financé conjointement par CANMET, les gouvernements provinciaux et l'industrie minière. Il a comme objectif le développement d'un inventaire de techniques qui pourraient servir à réduire l'impact environmental des résidus miniers et de la roche stérile, et d'éliminer le besoin de traiter les eaux de percolation.

Le projet Waite Amulet fait partie du programme et s'échelonne sur une période de cinq ans. Il vise à mieux faire comprendre les mécanismes hydrogéochimiques qui ont lieu au sein du parcs à résidus miners. La Phase 1 du projet (1985) comportait la reconnaissance du site et un programme de forages hydrogéologiques. L'étude hydrogéologique fut poursuivie au cours de la Phase 2, en même temps qu'une étude géochimique de la zone non-saturée. Des options de contrôle à être évaluées sur le terrain furent identifiées; on a procédé aussi à l'achat d'appareils de mesure de précipitation et des débits d'eau de surface et de percolation, afin de recueillir les données nécessaires au calcul du bilan hydrique et des charges de polluants.

Les travaux de terrain de 1987 (Phase 3) furent motivés par quatres objectifs: i) l'installation des nouveaux appareils; ii) l'étude des relations entre la minéralogie et la chimie de l'eau dans la zone non-saturée; iii) l'évaluation du degré d'entrée de l'oxygène à l'intérieur des résidus par diffusion; et iv) faire le suivi de l'écoulement et de la chimie de l'eau dans la zone saturée.

Le travail suivant fut accompli: i) l'installation du système de mesure de débit et de précipitation et le recueil d'une quantité limitée de données; ii) l'évaluation de l'altération minéralogique par M. J. Jambor de CANMET et une étude poussée de la chimie de l'eau dans la zone non-saturée par M.D. Blowes de l'Université de Waterloo (un rapport supplémentative sur les relations entre la chimie de l'eau et la minéralogie sera disponible vers la fin de 1988); iii) la mesure de profils d'oxygène des endroits avec et sans végetation de même qu'en des endroits recouverts d'argile; iv) mesures de conductivité hydraulique et de niveaux piézométriques et analyse des paramètres physico-chimiques en zone saturée.

Les recommandations pour le travail futur sont de: i) faire le suivir annuel du bilan d'eau et de métaux dissous; et ii) concentrer les travaux d'hydrogéologie le long des parois latérales du parc à résidus.

1. INTRODUCTION

1.1 Work Conducted in 1985-1986 (Phases 1 and 2)

The hydrogeochemical investigation of the reactive sulphide Waite Amulet tailings is part of the Reactive Acid Tailings/Wasterock Stabilization (RATS) Program which is jointly funded by Canada Centre for Mineral and Energy Technology (CANMET), the provinces and the mining industry. The overall objective of the RATS Program is to eliminate the need for perpetual maintenance and water treatment for reactive tailings (and wasterock) areas. Achievement of this objective will require the development of a better understanding of the biohydrogeochemical processes and controlling mechanisms. Based on this understanding, improved long-term tailings management practises can be developed.

In 1985, the RATS Program approved in principle a hydrogeochemical investigation of the Waite Amulet tailings site (illustrated in Figure 1), estimated to be a five-year $500,000 project to be funded equally by Noranda Inc. and CANMET. In 1985, a contract for Phase 1 (DSS File No. 23SQ.23440-5-9120) was issued to Noranda Research for $50,000 to conduct a preliminary site reconnaissance and drilling program([1]). In 1986, a $225,000 contract for Phase 2 (DSS File No. 23440-6-9099/01-SQ) was issued to Noranda Research to complete the definition of the site hydrogeology and evaluate the geochemistry of the unsaturated zone([2]). Work conducted by CANMET([3,4]) indicated that for one borehole, the pyrrhotite and pyrite were strongly altered in the unsaturated zone (above the water table) and an examination of 31 samples in the saturated zone([5]) showed minimal to no pyrrhotite alteration. The unsaturated zone (pore water and pore gas) investigated by D. Blowes (report appended to Reference 2) indicated pore water pH generally less than 3 with elevated metal levels (Fe^{2+} range 4-11,400 mg/L), and gaseous O_2 penetration was generally limited to less than 1 m depth. The saturated zone water had a pH generally greater than 5 with elevated metal levels (Fe^{2+} range 2-6000 mg/L). The elevated metal levels were above and below the water table and decreased with depth below the water table. The report's recommendations were incorporated into the Phase 3 proposal.

1.2 Scope of Work for 1987 (Phase 3)

In August 1987, a $75,000 contract for Phase 3 (DSS File No. 23440-7-9161/01-SQ) was issued to Noranda Research. The Statement of Work is attached as Appendix A.

The third year of the multi-year field study was to:

a) Develop a water and metal balance for the tailings site by monitoring precipitation, evaporation, the flow and water quality of the western seepage face and overland flow at the northern section. This included installation and checkout of the instrumentation purchased as part of Phase 2.
b) Relate the mineralogy to the unsaturated zone pore water geochemistry.
c) Evaluate oxygen diffusion into the tailings via determination of oxygen profiles at areas with varying cover characteristics.
d) Monitor pore water movement and geochemistry of the site, via sampling of established piezometers.

Investigation of the mineralogy was conducted by J. Jambor of CANMET, Mineral Sciences Laboratory, Ottawa. The unsaturated zone geochemistry is being examined in detail by D. Blowes as part of his doctoral work at University of Waterloo, and will be reported by him in 1988. The remainder of the work undertaken in this contract was by Noranda Research personnel.

2. METHODS OF INVESTIGATION FOR THE 1987 PROGRAM

2.1 Monitoring of Flow and Metal Loadings

Two monitoring stations were installed in July at locations illustrated in Figure 2. Station 1 was located on the top of the northern tailings section to monitor precipitation, evaporation and surface runoff (quantity and quality). Station 2, located along the western seepage face, monitored seepage quantity and quality of the western half of the main tailings dam.

The monitoring stations were designed to collect the data required for calculating water budgets and metal balances. Precipitation and evaporation were monitored to

assess water available for infiltration and runoff. Because overland flow from the 40 hectare site could only exit from the northern edge of the tailings, Monitoring Station 1 was installed there to assess runoff flowrate and quality. The 1985 examination of the geochemistry and hydrogeology indicated that the majority of pore water reports to the perimeter of the tailings dam. Monitoring Station 2 was installed to assess seepage rates and water quality of the western half of the dam seepage discharge. (It is assumed that this would be representative of the seepage for the whole dam).

The field data acquisition system for the overland and seepage flow monitoring Stations 1 and 2 is illustrated in Figure 3. The data were gathered at each station in two separate 32 k byte memory data loggers (Lakewood Model LE8305C) at 10-minute intervals. The flow rates were monitored at the two stations using Lakewood float pot water level recorders in Hinde Engineering Accura-flow H flumes (0.4572 m flume for Station 1 and 0.3048 m flume for Station 2). The height of the water in the flumes was transmitted as an analog signal to the data loggers.

A 24-bottle American Sigma Model 6201 automatic sampler, installed at each location, collected water samples at a preset interval controlled by the volume of water passing through the flume. This particular volume proportional sampling schedule was implemented in order to get more information on water quality during high flow periods (i.e. rainfall events) as compared to baseflow periods. A 475 mL sample bottle in the automatic sampler, pre-filled with 220 mL of distilled water and 5 mL of reagent grade hydrochloric acid, was used to collect the sample. This distilled water was used to minimize acid evaporation, and resultant corrosion of the automatic sampler.

A Signet pH monitoring sensor was installed at the exit of each flume in order to monitor pH changes, sending an analog signal between 0.5 and 2.5 volts, which corresponded linearly to pH values ranging from 2 to 14. This piece of equipment was the only component which did not perform satisfactorily. The pH readings were very unstable, possibly because of the rapid coating of the electrodes with iron hydroxide precipitates. Efforts will be made to solve this problem in the following phase of the study, which will include daily cleaning of the electrode.

The meteorological station installed at Station 1 consisted of an OTA 34-T tipping

bucket rain gauge and a Qualimetrics Model 6844-A evaporation gauge combined with an evaporation pan (approx. 1.2 m dia.). Rainfall events were recorded in the data logger as pulse signals accumulated for the number of tips (one tip = 0.2 mm of rain) encountered during each 10-minute interval. The evaporation flux was recorded by measuring the water level in the evaporation pan with a float system, which sent an analog signal between 0 and 5 V to the data logger, corresponding to a water level range of 0 to 125 mm of water in the pan.

All the data accumulated in the data loggers were retrieved at 5 to 15-day intervals by downloading to a Toshiba 1100 portable computer, using Lakewood software. Due to delivery delays and equipment problems, the two monitoring stations (illustrated in Figure 3) were not installed and functioning until mid-September. The equipment was decommissioned for the winter in October, prior to the hunting season. Data were only collected for a 20-day period, from 16 September to 6 October.

Sampling bottles were regularly replaced; a total of 26 samples were submitted for analysis (Fe^{2+}, Fe_T, Cu, Pb, Zn, Ca, Mg and SO_4).

2.2 Tailings Mineralogy

An investigation of the unsaturated zone tailings mineralogy was undertaken by J. Jambor([6]) of CANMET to characterize the alteration intensity and alteration products on core samples collected from the unsaturated zone by D. Blowes of the University of Waterloo during the 1986 field season. The core samples were collected by driving a 7.62 cm thin-walled aluminum tubing into the tailings with a percussion drill. The tubing was pulled out with the aid of a block and tackle. The samples were collected at Boreholes 2, 8, 11, 17, 20, 21, 22 and 24, illustrated in Figure 2. Core samples from Borehole 20, previously studied by Jambor([4]), were included in the mineralogical evaluation. Core samples and sample preparation are discussed in detail by D. Blowes (Reference 2, Appendix C) and J. Jambor (Reference 6, included as Appendix B in this report).

2.3 Oxygen Profiles, Tailings Moisture Content and Grain Size Distribution

A grid pattern, illustrated in Figure 4, was established over the 40 ha site to monitor oxygen profiles with depth, and tailings moisture content and grain size distribution. To monitor the extent of oxygen entry into the tailings, 1 cm diameter stainless steel tubes fitted with brass tips were hammered into the tailings to different depth intervals and pulled back to allow pore gas entry between the tip and the end of the tube. In areas where tailings were cemented, a portable hand drill with 61 cm long, 0.64 cm diameter bit was used to drill through the cemented tailings. The tubing and brass tip was then installed and hammered to the desired depth. The inner annulus of the stainless steel tubing was filled with a polyethylene tube to reduce the required pore gas volume for sampling.

The tailings particle size and moisture content were measured on core samples collected using a hand-held auger at locations adjacent to O_2 pore gas sample stations. The tailings core samples were split and dried for 24 h in an oven at $90^{o}C$. One half was used to determine moisture content. The remaining half of the dried sample was sieved to determine % passing on 208, 147, 104, 74, 52, and 45 micron screen, and d_{50} was established (where d_{50} is the 50% passing particle diameter, or median size).

2.4 Hydrogeology

Seventy-four piezometers were installed on site during the 1985 and 1986 field seasons. The piezometers were distributed in 26 stations located as shown on Figure 2. The 1987 hydrogeological monitoring program was executed as recommended by Blackport([2]) and consisted of monitoring water levels in piezometers on a weekly basis from May to August, and completion of the hydraulic conductivity testing of the piezometers.

Water levels were measured with reference to the piezometer collar, using a coaxial cable water level measuring tape. Hydraulic conductivity testing was performed using the Hvorslev rising head test. For a description of the piezometer design and installation procedure, the reader is referred to the reports by Blackport appended to the previous Noranda Research field reports([1,2]).

2.5 Saturated Zone Pore Water Sampling

All 74 piezometers were sampled twice (June and September) during the 1987 field season. To ensure fresh samples, the piezometers were emptied and allowed to refill prior to sampling. Piezometers less than 8 m were emptied and sampled using a peristaltic pump. For depths greater than 8 m, a nitrogen-driven positive displacement purge pump or a hand-operated bailer was used.

The pump discharge was connected to a 0.45 µm (ACRO 50A) disposable filter. In some instances, the pump disturbed the sediment at the piezometer tip, resulting in high suspended solids which would clog the filter; the samples were first poured into a bottle to settle the sediments, and the supernatant was then filtered.

A split of the filtered sample was used for field determinations of temperature, electrical conductance (Ec), pH, redox potential (Eh), acidity and ferrous iron concentrations. The remainder of the sample was fixed with reagent grade HCl (1% v/v) and submitted to the Noranda Environmental Laboratory for analysis of Fe_T, Cu, Pb, Zn, Ca, Mg, and SO_4.

Four suction lysimeters that were installed in 1986 at Stations 20 and 24 were pumped in order to obtain pore water samples from the unsaturated zone. Only one of the lysimeters was successfully sampled. The difficulty in obtaining samples in the three remaining instruments may have been because the sand pack around the porous cup was too coarse. This will be resolved prior to further installations.

2.6 Quality Assurance and Control Program

Several measures were taken to minimize saturated zone piezometer sample contamination:

- Sampling equipment, which included the sample tubes and hand-operated bailer, were rinsed with distilled water prior to sampling each piezometer.

- Each filter was disposed of after one use.

- Sample tubes were not allowed to touch the tailings and were hung up when not in use.

Quality control of analytical results was assessed with the use of replicates, blanks and spikes. Replicate determinations, illustrated in Table I, are from piezometers 19-1 and 25-1 for June sampling and 17-1 and 13-2 for the September sampling round. In general, the reproducibility for concentration >1 mg/L for Fe, Cu, Pb, Zn, Ca, Mg and SO_4 was good since the coefficient of variation was low (<10%). Coefficient of variations were high (111%, 34%, 114%, 85% and 39%) for low level concentrations of <1 mg/L of Cu, Pb, Zn and Ca.

To determine reproducibility of the pore water sample, piezometers 4-1 and 5-2 were purged, sampled and allowed to refill. This procedure was repeated four times. The results, illustrated in Table I, indicate good reproducibility since the coefficient of variation is generally <10%.

The field blank samples, detailed in Table II, were distilled water which was passed through the sampling equipment to assess contamination in the sampling method. Contamination was mainly Fe at levels <0.1 mg/L. The field blank results were comparable to the blank results also shown in Table II.

The spiked samples shown in Table III were required to assess reproducibility, accuracy and bias in the analysis. The accuracy for Fe_T was also good (Relative Error <5%).

3. RESULTS AND DISCUSSION OF 1987 FIELD PROGRAM

3.1 Monitoring of Flow and Metal Loadings

The following results are based on data collected for a 20-day period, from 16 September to 6 October. They provide only a preliminary assessment of flow and metal concentrations.

Station 1 - Evaporation and Precipitation

The evaporation results (Figure 5a) to Day 15 indicate a range of 0-3 mm/d, for a total for that period of 25 mm. The total rainfall was 70.8 mm in the 20-day period (illustrated in Figure 5b), distributed as follows:

Day	3-4	6	7	8	9	12-13	15	16	18
Rain (mm)	13.4	0.4	0.2	0.4	0.4	22.6	19.8	7.0	6.6

Station 1 - Flow

There was no surface flow to the north via this station until after the major rain on Day 18. The majority of the flow is likely to occur during the spring due to snow melt and high water table conditions.

Station 2 - Flow

Monitoring Station 2 receives overland flow from about 3.5 ha surface along the bench plus seepage from an approximately 20 ha section of the tailings dam. As illustrated in Figure 5c, the total flow for the 20-day period was about 1520 m^3. The pattern of flow was as follows:

- Initial baseflow condition was 1.9 m^3/h of seepage.
- Rain events on Days 3-4 increased the peak flow to about 20 m^3/h, followed by a gradual decline to about 1.4 m^3/h on Day 10.
- Rain on Day 12 caused a peak flow of 43 m^3/h, with subsequent declines between events to the initial base flow condition.

Quality Changes

Twenty six samples from the automated sampler were analyzed for Fe_T, Fe^{2+}, Cu, Zn, Ca, Mg and SO_4 (Table IV). The results for Fe_T and Fe^{2+}, illustrated in Figure 6a, ranged from 1-1.7 g/L to 0.4-1 g/L, respectively. The results on Day 4 and 13 indicate peak loadings for Fe just after peak flows. This may be due to flushing of the oxidized products within the tailings adjacent to the seepage ditch and/or re-suspension of iron hydroxides from the bed of the seepage ditch.

The Fe_T loadings are illustrated in Figure 6b. At the base flow of 1.9 m^3/h, the loading was 3 kg/h Fe_T, while at the peak flow rate of about 32 m^3/h, the loading was 28 kg/h Fe_T. Figures 6c and 6d illustrate concentration and loading versus flow. Under low flow conditions (<4 m^3/h, which is considered base flow), Fe_T concentrations range from 1.2 to 1.5 g/L. During precipitation events, rainfall will report to Station 2 by:

- directly falling into the ditch;
- running overland over the 3.5 ha into the ditch;
- along the upper bench, infiltrate to the water table and report as seepage to the ditch;
- along the lower bench, the seepage face will rise and infiltrating rainfall report to the seepage face.

To further delineate the loadings to flowrate, more sampling will be required during rainfall events. This will be accomplished by reducing the volume between sampling during rainfall events.

3.2 Tailings Mineralogy

The mineralogical examination of 31 core samples from the saturated zone conducted by J. Jambor([3]) indicated only local alteration of pyrrhotite grains which would have taken place during the operating life of the tailings dam. As these tailings had been spigotted out, they would have been exposed for months prior to being covered by the next lift of tailings.

An initial examination of the mineralogy in the unsaturated zone by Petruk and Pinard([1]), which was later confirmed by Jambor([3]), at piezometer Station 20 indicated that a well-defined oxidized zone near surface was nearly depleted of sulphides, with 5% pyrite and no pyrrhotite; in an intermediate level above and at the water table, there was 25% pyrite and 6% pyrrhotite; and below the water table where there was minimum alteration, there was 60% pyrite and 14% pyrrhotite. The strongly oxidized zone exhibited a yellow or brownish-yellow colouring. Colour changed to black at depth, indicating unoxidized sulphide-rich zones.

A more detailed assessment of the unsaturated zone mineralogy was conducted by Jambor([5]) to assess the alteration intensity and products of alteration. The alteration intensity is an index defined as follows:

10	=	all pyrite and pyrrhotite is oxidized
9	=	a few grains of pyrite remain
7-8	=	a minor amount of pyrrhotite remains
7 and less	=	decreasing degree of pyrrhotite alteration

The following summarizes his work (detailed in Appendix A) on cores at piezometer Stations 1, 2, 8, 11, 17, 20 and 22. See Figure 7 for profiles of alteration intensity and chemical parameters. For Borehole 22 (coarse material with a low water table) the alteration intensity is very high in the first meter, while for Borehole 2 (finer material with a water table at 0.5 m), alteration is largely limited to the first 40 cm.

The water soluble fraction of the tailings contains $FeSO_4.nH_2O$ and $CaSO_4.nH_2O$ minerals. The oxidation of sulphides, mainly pyrite, pyrrhotite and magnetite, results in soluble Fe in the pore water. Minor amounts of Cu and Zn are found in soluble low pH water due to the oxidation of chalcopyrite, covellite and sphalerite. The water soluble Fe is depleted in the strongly oxidized unsaturated zone illustrated in Figure 7. The downward migration of Fe is indicated by elevated levels at depth. The Fe profile for Borehole 22 indicated a downward plume of Fe in the unsaturated zone, whereas at Borehole 2, the Fe plume was below the water table. This was consistent with the results reported by Blowes([4]). The highest value of elemental sulphur (S^0), a by-product of sulphide oxidation is found at the base of the highly oxidized zone. Insoluble sulphates are likely jarosite, which correlate well with the alteration intensity. A more detailed assessment of the unsaturated zone porewater and mineralogy is under investigation by D. Blowes and J. Jambor.

3.3 Oxygen Profiles, Tailings Moisture and Grain Size

Oxygen Profiles

Figure 8 illustrates three typical oxygen profiles for vegetated, bare and clay-covered tailings. For the first two, oxygen is generally consumed within the first 0.3-0.5 m of depth. Under clay cover (Stations B1, C2, C3, C9), the oxygen content remained relatively constant at about 20% until the tailings layer was reached, at which time a gradient was observed, indicating depletion of the oxygen by tailings reactions. In all cases, tailings change colour from yellow-brown to black correspond to decreased oxygen levels.

At seven of the 10 stations where hardpan was encountered (A8, B4, C1, D9, E1, E3 and E7), oxygen level was minimal at the hardpan layer. The exceptions were Stations A1, A2 and A3 which are along the road, close to the top berm; the higher oxygen level noted may be related to the lateral influx of oxygen and/or the physical characteristics of the tailings at this point (coarse-grained, cemented, difficult to penetrate with the probe). Detailed results of oxygen profiles are in Appendix C.

Moisture Content

The range of % moisture was 6-34%. Moisture levels generally decreased with depth. In the fine-grained areas, moisture decreases from 25% to 20% on average. For areas which are coarse-grained, the range moisture content was generally 20% near surface and decreasing with depth to between 6 and 10%. In both cases, moisture contents increase as the water table was reached. Detailed results of tailings % moisture profiles are in Appendix D.

Grain Size Distribution

The medium particle diameter, d_{50}, varied from 72 to 111 mcirons. The coarser tailings (>100 microns) are situated mainly along the berm, the result of spigotted dam construction with coarse tailings, and along the winter discharge point at Stations C1 and C2. Particle size with depth are illustrated in Appendix E, summarized with results of gaseous O_2 %, moisture %, grain size, colour and depth of sample. Work is currently underway to complete the grain size distribution curve for

the remaining stations, and develop relationships bewteen d_{50}, % moisture and O_2 profiles.

3.4 Hydrogeology

The main hydrogeological features of the tailings site as reported in the initial study by Blackport([1]) are:

- The tailings are lying on a 2 to 20 m thick clay layer. The elevation of the clay surface gently decreases to the south and west. The bedrock underneath the clay is of irregular surface and slopes to the south-southeast.

- The water table is just below surface in the north and central portions, where the tailings are fine-grained. The water table is deeper in the coarse-grained southern part of the site.

- Pore water flow occurs generally from the central part of the tailings towards the side, with a variably downward vertical component. The clay layer acts as a barrier to flow but discharge of tailings pore water to the bedrock is allowed where the clay layer is thin (northwest portion of site).

Data obtained during the 1987 field season were used to further define the hydrogeology.

Hydraulic Conductivity

The new hydraulic conductivity results are given in Table VI. Hydraulic conductivities in the tailings ranged from 1.21×10^{-3} to 2.23×10^{-6} cm/s. As in the preliminary study, the highest hydraulic conductivities (1×10^{-3} to 1×10^{-4}) were measured in piezometers located along the dam, where the tailings are coarse-grained. A trend of decreasing hydraulic conductivity with depth was evident at some piezometer nests, reflecting the effect of consolidation on the deeper parts of the tailings deposit. Some piezometer nests did not follow this trend; low permeability zones were observed all along the profile, probably corresponding to the "slime" lenses observed in the cores.

Measured hydraulic conductivities in the clay layer ranged from 5.16×10^{-4} to 5.58×10^{-7} cm/s. The lower hydraulic conductivity values were obtained in the thick clay in the south portion of the site. Much higher values were measured in the thin silty clay layer under the north portion of the site. The hydraulic conductivity values in the silty clay were comparable to the ones obtained in the fine-grained tailings and the deep, more consolidated tailings (roughly one order of magnitude difference only).

Hydraulic conductivities in the bedrock were 7.15×10^{-4} cm/s at Piezometer 2-5 and 6.19×10^{-5} cm/s at Piezometer 9-7. This reflects the original observations made by Blackport on the rock cores: chlorite-filled fractures with no noticeable high hydraulic conductivity zones at piezometer 9-7 and large highly conductive open fractures at Piezometer 2-5. The combined effect of fractured bedrock conductivity and thin clay base are factors that will promote downward migration of tailings water into the bedrock in the northwest portion of the tailings.

Water Table

Figure 9 shows water table configurations for May and August 1987. The water level on-site varied from 1.1 to 7.5 m below ground. As in the previous years, the lowest water levels were found in the south portion of the tailings, and the highest water levels were in the central part. Water table slopes were steep across the northwest and southeast portions of the tailings dam, and smoother elsewhere.

Comparison between water table surfaces of May and August reflect the difference with north and south portions of the site. In the south, where the tailings are coarse, rapid drainage occurs even in the wet spring season, and the water table configuration remains relatively unchanged through the summer. However, in the north end, the infiltration of spring runoff is stored much longer in the tailings, indicated by the presence of a water table mound in the north-central section and steeper gradients in the northwest section of the tailings.

Hydrographs along cross sections A-A and B-B (Figure 9) were chosen to illustrate this concept in Figure 10. Section A-A is typical of the south section of the tailings. Hydrographs of Piezometers 20 and 11 on this line remain relatively stable

through the whole period of study. On the other hand, water level hydrographs of piezometers 20, 11 and 24 along Section B-B in the north portion of the tailings show the groundwater storage accumulated during the wet season, with Station 9 draining progressively with time. Steady state conditions were not reached until Week 10 of the study period (and July). The rise of the water table was around 1 m and was observed from hydrographs at Stations 2, 3, 5, 6, 7, 8, 9 and 10, and to a lesser degree, at Stations 1 and 15.

Studies are proposed to use a groundwater flow computer model to quantify the flow system more accurately. The model would also show the effect of the observed mound in the water table on the fluxes entering the bottom stream. At the present time, preliminary estimates can be obtained using Darcy's equation with parameter values derived from flownets represented in Figures 11 and 12. This calculation gives a value for total discharge in the ditch of about 0.8 m^3/h. All uncertainties considered, this value compares well with the baseflow value in the stream of 1.9 m^3/h, computed in Section 3.1.

3.5 Tailings Pore Water Chemistry

Mineralogical examinations in the unsaturated zone by Jambor([2,4]), summarized in Figure 7, indicated complete oxidation of pyrrhotite and pyrite in the near surface zone and decreasing alteration with depth. An investigation of the unsaturated zone pore water geochemistry by Blowes([2]) confirms the presence of sulphide oxidation products, mainly low pH pore water with elevated levels of Fe^{2+} and SO_4^{-2}. This pore water will report to the tailings water table and exit to groundwater or report as seepage along the dam perimeter. To examine the extent of migration of the oxidized species in the saturated zone, piezometers were sampled in October 1986, June 1987 and September 1987. The three sampling rounds for Station 9 are compared graphically with depth in Figure 13. Typically, the pore water chemistry showed no major change during the one-year sampling period. Since the pore water is moving 1-5 m/a, it is unlikely that the pore water chemistry would change rapidly in the one-year sampling period. It is therefore recommended not to sample all the piezometers during the 1988 field program.

The highest Fe^{2+} levels were encountered in the tailings bench and in the central-west and southwest portions of the tailings deposit. The dissolved Fe^{2+} will travel

in solution following the prevailing hydraulic gradients. However, large amounts of Fe^{2+} were found in the coarser tailings piezometers 11, 25 and along the bench (piezometers 20, 27) of the sections, forming a high-level plume which is directly in contact with the drainage ditch. A more precise quantification of the flow systems in the study sections would allow the prediction of contaminant travel paths and travel times between the source and the outflow.

4. CONCLUSIONS

This study, funded by Noranda Inc.-CANMET as part of the RATS program, will assist industry in understanding the processes which control pore water evolution in sulphide tailings and develop improved tailings management methods.

The project is a multi-year study which will characterize the hydrogeochemistry of the abandoned Waite Amulet tailings site. Piezometers were installed to determine the pore water flow system and pore water evolution. Core samples were taken to determine the unsaturated zone pore water chemistry and mineralogical alteration of tailings solids. A gas sampling program was undertaken to determine the extent of diffusion into the tailings mass. Overland and seepage monitoring stations were established to determine the baseline flow and water quality at the site and variations due to rainfall events.

An investigation of the Waite Amulet tailings has indicated that the sulphide tailings have oxidized to a depth of approximately 1 m over the entire tailings site. Oxidation of sulphides has resulted in elevated metal levels in the tailings porewater, which reports to the water table and subsequently as seepage along the dam face.

Specific conclusions are:

a) The quality assurance results indicate that the water quality data are satisfactory regarding accuracy and reproducibility.

b) Definition of the tailings site hydrogeology is complete. An extensive set of piezometers has been installed and considerable data compiled regarding physical

details, flows and hydraulic conductivities. Further work would be focused on the seepage face and on modelling.

c) Porewater sampling and analysis has provided a basis for an integrated assessment of overall chemistry within the tailings area, including mineralogy and chemistry of the saturated and unsaturated zones.

d) The comprehensive evaluation of changes in tailings mineralogy by J. Jambor and porewater chemistry by D. Blowes has provided a solid input for evaluating the chemistry of the and unsaturated zones. Detailed review of this work is scheduled for late 1988.

e) Oxygen profiles indicate that oxygen is rapidly consumed in bare or vegetated tailings. Under the clay cover, the oxygen level remained constant within clay covers until the tailings layer is reached. Oxygen is typically depleted at the hardpan layer when one is present.

f) Initial results from monitoring Stations 1 and 2 for a 20-day period provided evaporation, precipitation, surface water, seepage flow and quality. No overland flow was recorded at Station 1. Station 2 experienced a base flow ~2.0 m^3/h with an Fe_T range from 1.3-1.5 g/L. During rainfall events, Fe_T would drop to <1 g/L.

5. RECOMMENDATIONS

Monitoring Flow and Quality

The 1987 field program provided limited water quality data with rainfall events for Station 2 and no data for Station 1. Further data are required to:

- Determine overland flow (runoff versus infiltration) and water quality for Station 1.
- Assess baseflow loadings and dilution during rainfall events for Station 2.
- Determine the metal loadings from seepage versus overland flow.

Hydrogeochemical Study Along Seepage Face

Pore water flow and quality data between the western bench and seepage ditch is limited. Further work would include:

- Install piezometers and suction lysimeters along three sections of the western dam.
- Determine pore water flow regime.
- Determine the geochemical profile.

Integrated Assessment of Overall Chemistry

J. Jambor and D. Blowes are currently assessing the unsaturated zone mineralogy and pore water chemistry. The outcome of this work will be incorporated into an overall assessment of the site, which will be prepared in cooperation with them and issued by Noranda Research in late 1988, as part of this contract.

Modelling

Flow modelling is recommended for the Waite Amulet site, particularly along the bench face to determine flow contributions from infiltration, seepage and storm flow.

The Reactive Acid Tailings Assessment Program Model (RATAP) was prepared specifically for modelling high sulphides. Senes Consultants are currently validating the model using Waite Amulet data. Further validation of this model is recommended using the most recent field data.

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TABLE I

QUALITY CONTROL, REPLICATE DETERMINATIONS OF WAITE AMULET PIEZOMETER SAMPLES, 1987

	Fe^{++} mg/L	Fe_T mg/L	Cu mg/L	Pb mg/L	Zn mg/L	Ca mg/L	Mg mg/L	SO_4^{-2} mg/L
(Piezometer 19-1)								
Replicate 1								
June	18	18.3	<0.02	<0.05	0.02	252	168	2200
	22	22.5	<0.02	<0.05	0.02	260	203	2000
	18	18.6	<0.02	<0.05	0.20	275	211	2200
	18	18.8	<0.02	<0.05	0.20	253	196	2200
	18	18.2	<0.02	<0.05	0.01	257	196	2200
$\bar{X}$ (mg/L)	18.00	19.00	<0.02	<0.05	0.09	213	194	2200
S.D. (mg/L)	1.70	1.80	-	-	0.10	106	16	89
C.V. (%)	9.52	9.42	-	-	111	50	8	4
(Piezometer 25-1)								
Replicate 2								
June	4000	4035	<0.02	<0.05	0.22	389	2188	15500
	3600	4015	0.03	0.17	0.21	367	2213	14500
	4000	4200	0.04	0.14	0.22	367	2004	16000
	2700	4100	<0.02	0.10	0.21	367	2121	15500
	4100	4470	<0.02	0.70	0.21	397	2179	15000
$\bar{X}$ (mg/L)	3880	4164	0.026	0.23	0.21	377.4	2141	15300
S.D. (mg/L)	216	185	0.01	0.27	0.01	14.0	83	570
C.V. (%)	5.59	4.46	34.40	114.42	2.56	3.85	3.91	3.73
(Piezometer 17-1)								
Replicate 3								
September	7.7	7.89	<0.02	<0.05	0.01	335	337	2900
	8.6	8.87	<0.02	0.08	0.01	360	370	3600
	8.5	8.51	<0.02	<0.05	0.01	342	337	3800
	8.8	8.83	<0.02	0.08	0.01	324	325	3800
	9.0	9.00	<0.02	0.06	0.01	355	359	3200
$\bar{X}$ (mg/L)	8.5	8.62	-	0.044	0.01	343	345	3460
S.D. (mg/L)	0.50	0.45	-	0.04	0.00	14.60	18.3	390
C.V. (%)	5.83	5.18	-	-	0.00	4.27	5.31	11.49
(Piezometer 13-2)								
Replicate 4								
September	2150	2150	0.02	0.12	0.06	264	627	7400
	2310	2010	0.02	0.12	0.06	354	855	6800
	2000	2347	0.02	0.13	0.10	318	748	7400
	2100	2000	0.09	0.15	0.06	371	877	6600
	2010	2100	0.03	0.12	0.13	363	827	6800
$\bar{X}$ (mg/L)	2114	2121	0.036	0.12	0.08	334	786	7000
S.D. (mg/L)	126	140	0.03	0.01	0.03	44	101	374
C.V. (%)	5.97	6.64	84.71	10.19	38.95	13.19	12.94	5.35
(Piezometer 4-1)								
4-1a	4800	4800	0.08	0.24	56.3	204	829	2100
4-1b	5600	5630	<0.02	0.33	60.7	186	963	8800
4-1c	4800	5400	<0.02	0.3	53.8	186	927	9400
4-1d	5000	5450	<0.02	0.3	54.1	189	909	8800
$\bar{X}$ (mg/L)	5050	5320	-	0.29	56	191	907	7275
S.D. (mg/L)	378	360	-	0.04	3.19	8.6	56.6	3461
C.V. (%)	7.5	6.78	-	12.9	5.67	4.5	6.2	47.6
(Piezometer 5-2)								
5-2a	125	125	<0.02	0.06	0.01	294	173	1700
5-2b	125	125	<0.02	<0.05	0.02	298	186	1700
5-2c	128	128	<0.02	<0.05	0.03	282	174	1700
5-2d	144	144	<0.02	<0.05	0.03	238	152	1900
$\bar{X}$ (mg/L)	130	130	-	-	0.02	278	171	1750
S.D. (mg/L)	9.1	9.1	-	-	27.5	141	14.1	100
C.V. (%)	6.98	6.98	-	-	42.6	9.9	8.25	5.71

$\bar{X}$ = Arithmetic Mean, mg/L
S.D. = Standard Deviation, mg/L
C.V. = Coefficient of Variation, %

TABLE II

QUALITY CONTROL, WAITE AMULET FIELD BLANKS AND REPLICATE SAMPLING, 1987

	Fe^{++} mg/L	Fe_T mg/L	Cu mg/L	Pb mg/L	Zn mg/L	Ca mg/L	Mg mg/L	SO_4^{-2} mg/L
Field Blank								
June	0.1	0.26	<0.02	<0.05	<0.10	1.46	2.5	<0.1
"	0.1	0.10	<0.02	<0.05	<0.10	0.73	0.48	<0.1
"	<0.1	0.09	<0.02	<0.05	<0.10	<0.50	<0.2	<0.1
"	<0.1	0.12	<0.02	<0.05	0.02	<0.50	<0.2	<0.1
"	<0.1	0.09	<0.02	<0.05	0.02	0.73	0.2	<0.1
"	<0.1	0.16	<0.02	<0.05	0.01	<0.50	<0.2	<0.1
September	0.2	0.71	0.02	<0.05	0.01	1.66	3.44	7.0
Blank								
June	<0.1	<0.05	<0.02	<0.05	0.02	<0.5	<0.2	<0.1
"	<0.1	<0.05	<0.02	<0.05	<0.01	<0.5	<0.2	<0.1
"	<0.1	<0.05	<0.02	<0.05	0.01	<0.5	<0.2	<0.1
September	<0.1	0.49	<0.02	<0.05	0.01	1.27	2.87	3
"	<0.1	0.05	<0.02	<0.05	0.01	2.27	0.8	3
"	<0.1	0.09	<0.02	<0.05	<0.01	1.36	3.77	3

TABLE III

QUALITY CONTROL, WAITE AMULET SPIKED SAMPLE ANALYSES, 1987

SERIE No.	June	June	Sept.	Sept.	Sept.
Fe TRUE VALUE mg/L	5	50	50	100	500
	4.99	48.8	49.4	100	
	4.94	49.3	48.2	96.1	489
Replicate	4.75	49.6	51.9	96.7	517
Analysis	5.46	49.8	48.3	96.5	489
	4.81	49	50	94.9	426
X	4.99	49.3	49.6	96.8	480.3
S.D.	0.28	0.41	1.51	1.90	38.5
C.V.	5.61	0.84	3.05	1.96	8.02
R.E.	0.2	1.4	0.88	3.16	3.95

X = Arithmetic Mean
S.D. = Standard Deviation
C.V. = Coefficient of Variation
R.E. = Relative Error

TABLE IV

ANALYTICAL RESULTS FOR SAMPLES COLLECTED BY AUTOMATIC SAMPLER AT STATION 2, WAITE AMULET, 16 SEPTEMBER TO 6 OCTOBER 1987

Date	Time	Cu mg/L	Pb mg/L	Zn mg/L	Fe_T mg/L	Fe^{2+} mg/L	SO_4 mg/L	Ca mg/L	Mg mg/L
Sept. 17	05:20	0.85	0.14	4.47	1447	941	6264	357	695
" 18	03:00	0.85	0.19	4.23	1473	993	7091	364	723
" 19	00:00	0.72	0.12	3.62	1274	881	6264	305	609
" 19	21:10	0.72	0.16	3.64	1382	902	6300	360	732
" 20	19:50	1.04	0.00	4.38	1693	920	6264	346	650
" 20	22:40	1.45	0.20	4.30	10918*	624	4912	274	397
" 21	01:50	1.80	0.16	6.00	1420	902	5600	314	538
" 21	19:20	1.06	0.12	4.68	1306	846	8000	328	606
" 22	16:10	1.06	0.12	4.62	1276	708	9200	338	628
" 23	13:00	0.91	0.19	4.31	1345	820	6914	304	585
" 24	10:30	0.88	0.24	4.40	1496	932	7200	342	672
" 25	14:50	0.78	0.30	4.24	1428	902	6800	328	666
" 26	12:30	0.78	0.27	4.01	1416	925	7367	323	653
" 27	20:10	0.70	0.24	3.72	1326	804	6800	312	652
" 29	09:30	1.16	0.12	3.78	1134	630	5800	254	432
" 29	11:50	1.64	0.16	5.30	1310	759	5935	276	436
" 29	14:00	1.60	0.16	3.84	868	384	3600	242	276
" 29	21:50	1.44	0.24	4.32	1144	640	4500	268	392
" 30	11:00	1.31	0.12	4.83	1300	767	4809	321	555
Oct. 1	08:50	1.15	0.16	4.96	1400	936	6133	293	541
2	05:00	1.49	0.36	4.89	1275	761	4615	235	382
2	08:00	1.72	0.26	4.67	1040	588	4954	224	310
2	11:50	1.93	0.27	5.54	1156	633	5559	248	375
2	21:10	1.72	0.28	5.47	1191	694	5600	261	414
3	14:20	1.64	0.22	5.58	1273	691	5815	295	493
4	20:00	1.20	0.00	4.77	1227	776	6023	310	464

* Considered as an outlier.

TABLE V

HYDRAULIC CONDUCTIVITIES OF PIEZOMETERS
INSTALLED IN 1986 FIELD SEASON

Piezometer	Hydraulic Conductivity K (cm/sec)	Surrounding Material
2-5	7.15E-04	bedrock
4-3	1.52E-04	tailings
4-4	1.21E-03	tailings
9-6	5.16E-04	clay
9-7	6.19E-05	bedrock
10-1	1.22E-05	tailings
15-3	8.56E-05	clay
15-4	2.23E-06	tailings
17-6	1.20E-06	clay
18-1	5.58E-07	clay
18-2	6.33E-05	tailings
24-1	8.59E-06	tailings
24-2	1.78E-05	tailings
24-3	2.48E-05	tailings
24-4	5.94E-06	tailings
24-5	1.09E-05	tailings
25-1	9.71E-05	tailings
25-2	5.12E-05	tailings
26-1	2.38E-05	tailings
26-2	1.48E-05	tailings
26-3	5.78E-04	tailings
26-4	6.88E-05	tailings
27-1	2.86E-04	clay
27-2	9.92E-05	tailings
27-3	1.82E-04	tailings

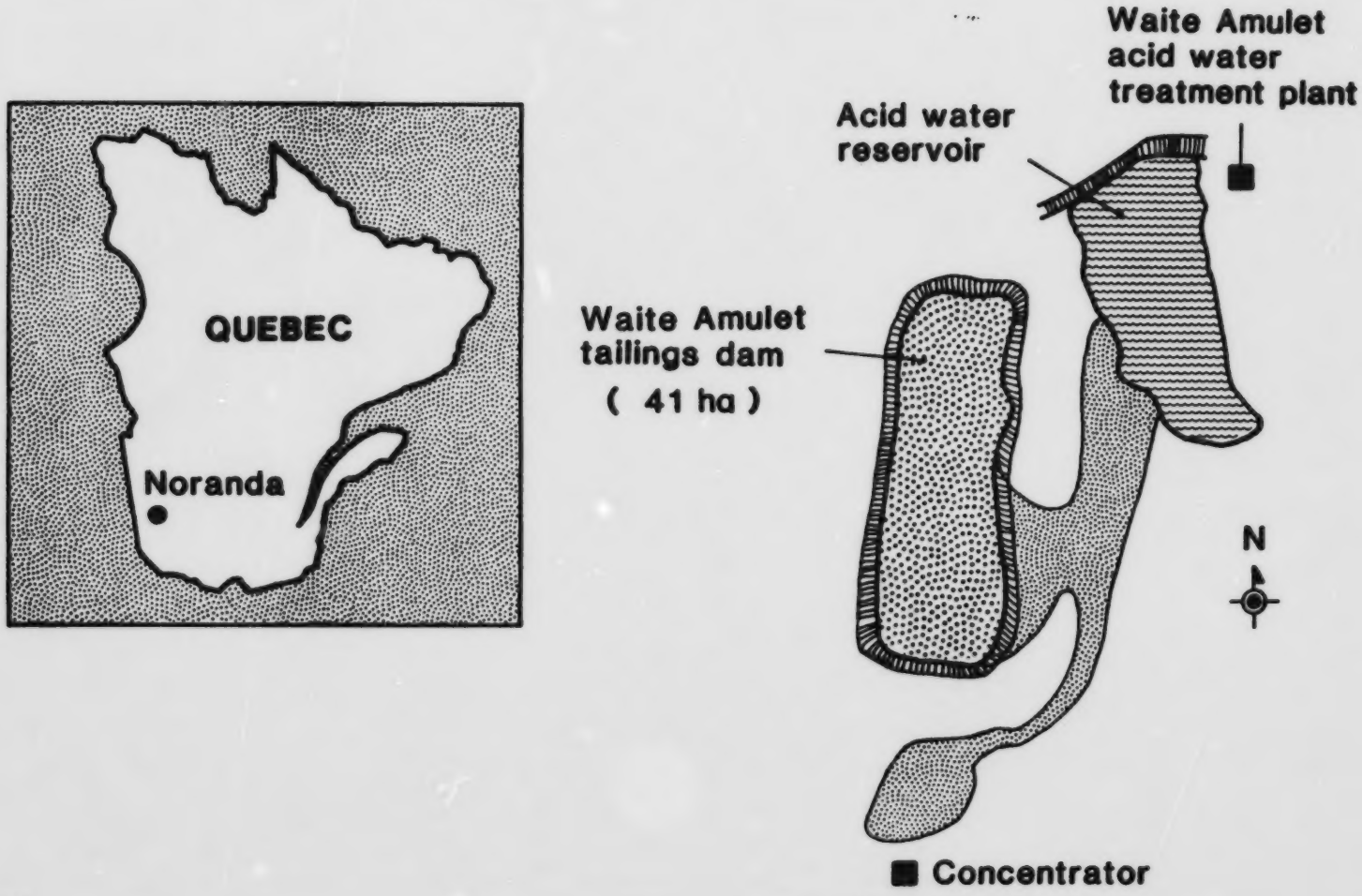


Figure 1 - Location of Waite Amulet Tailings

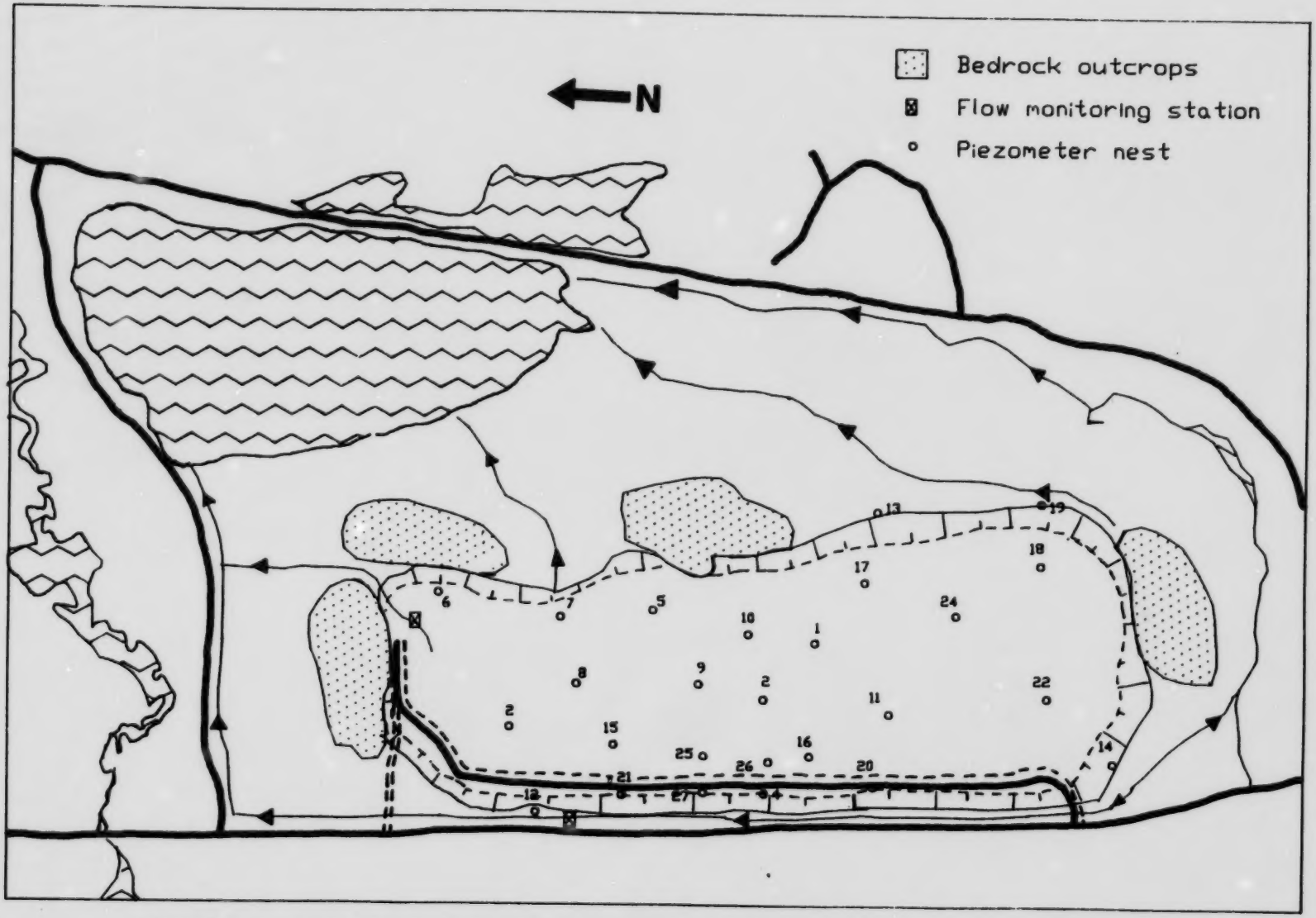


Figure 2 - Location of Piezometer Nests and Flow Monitoring Stations, Waite Amulet Tailings Site

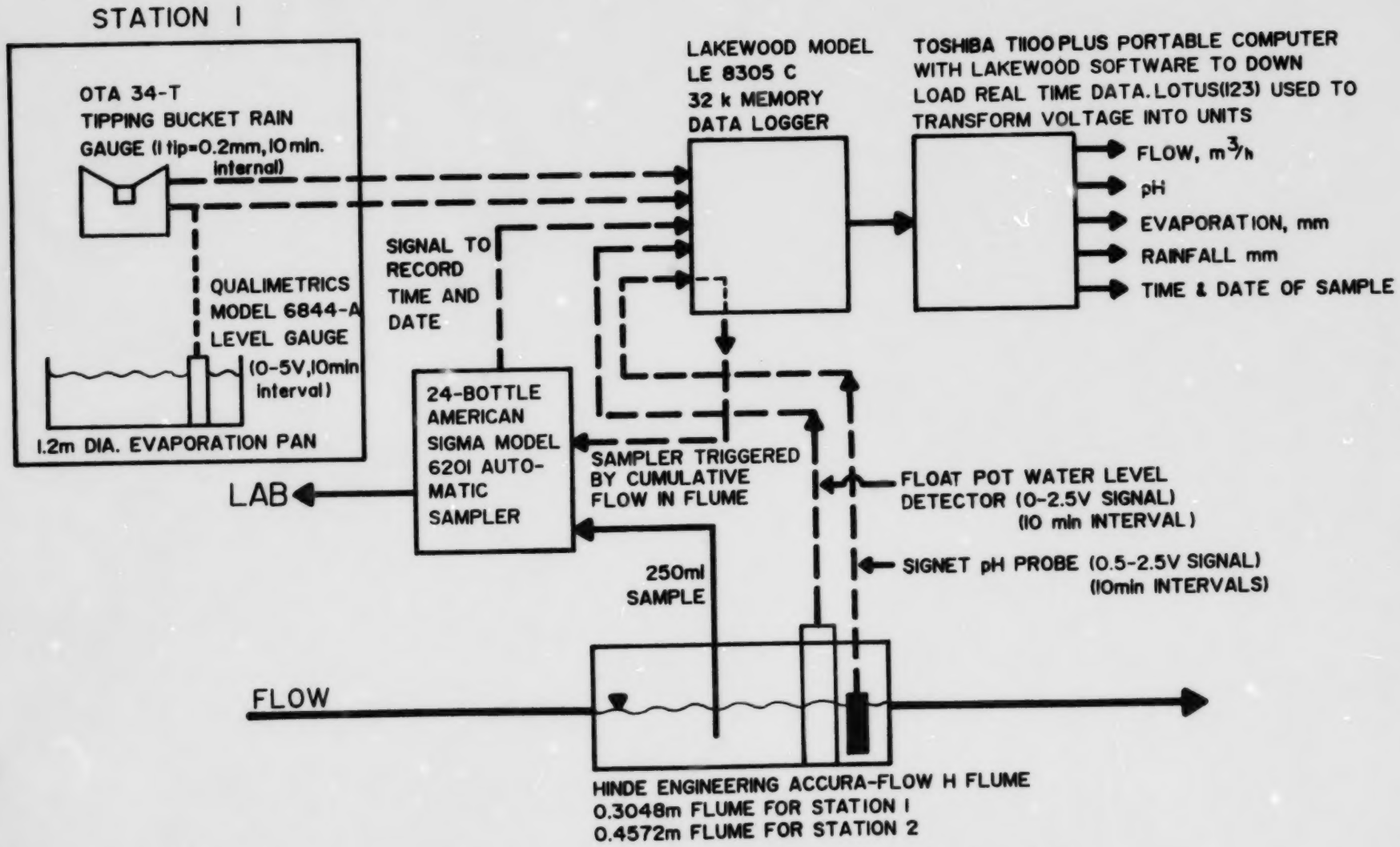


Figure 3: Flowsheet for monitoring stations 1 and 2

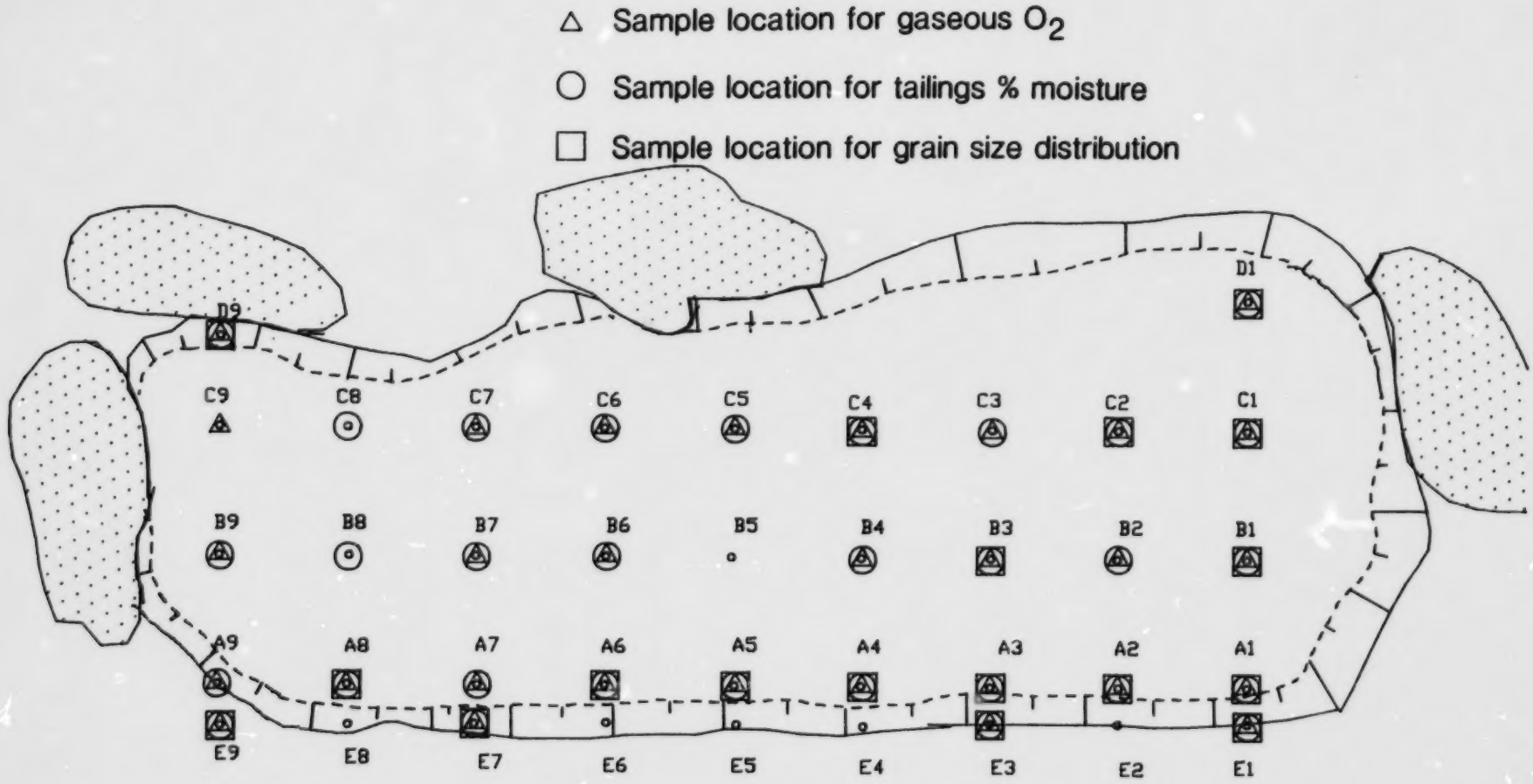


Figure 4 - Location of Pore Gas, Moisture Content and Grain Size Sampling Stations

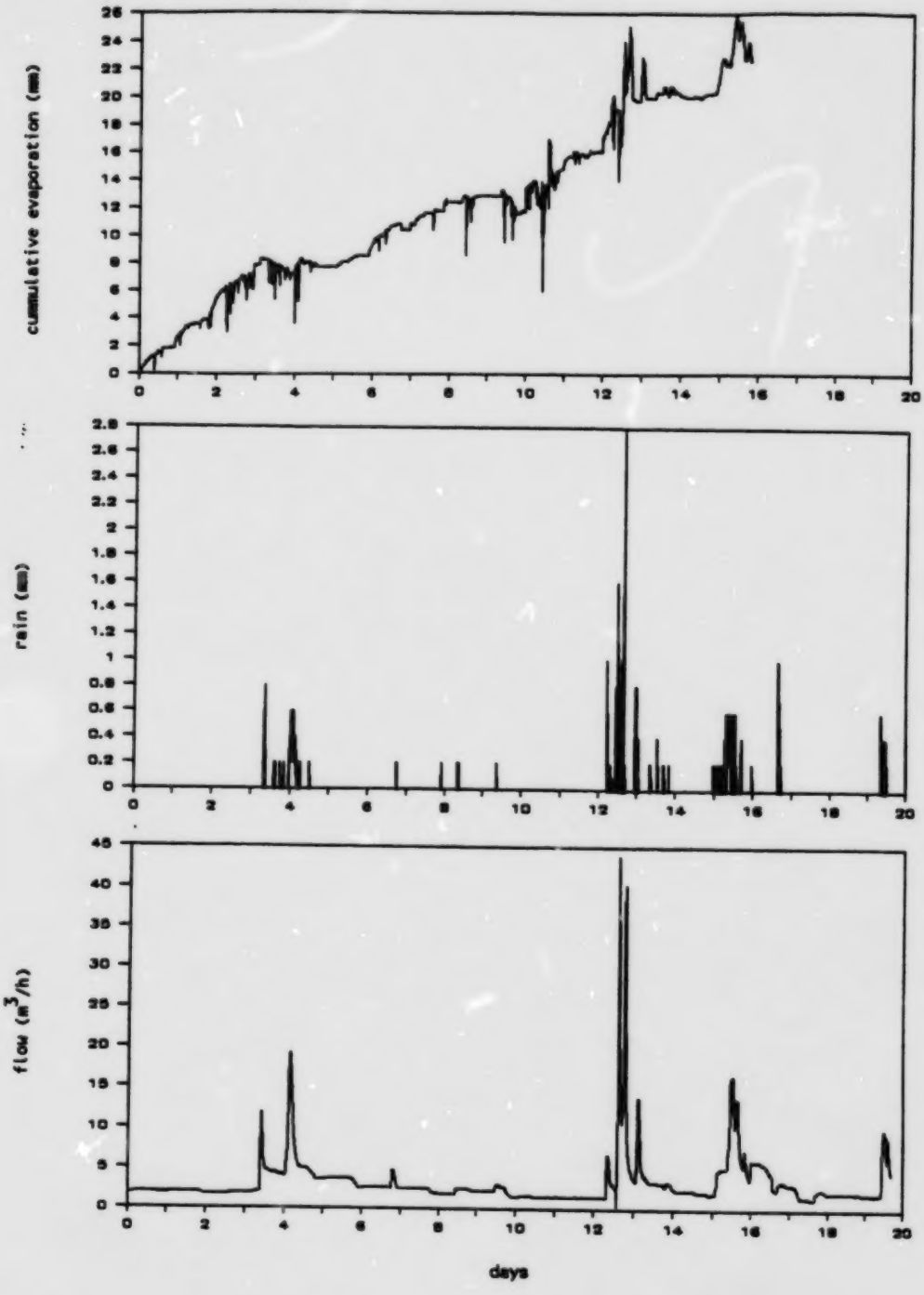


Figure 5 - Evaporation, Precipitation and Flow for Waite Amulet Tailings, 16 September to 6 October 1987

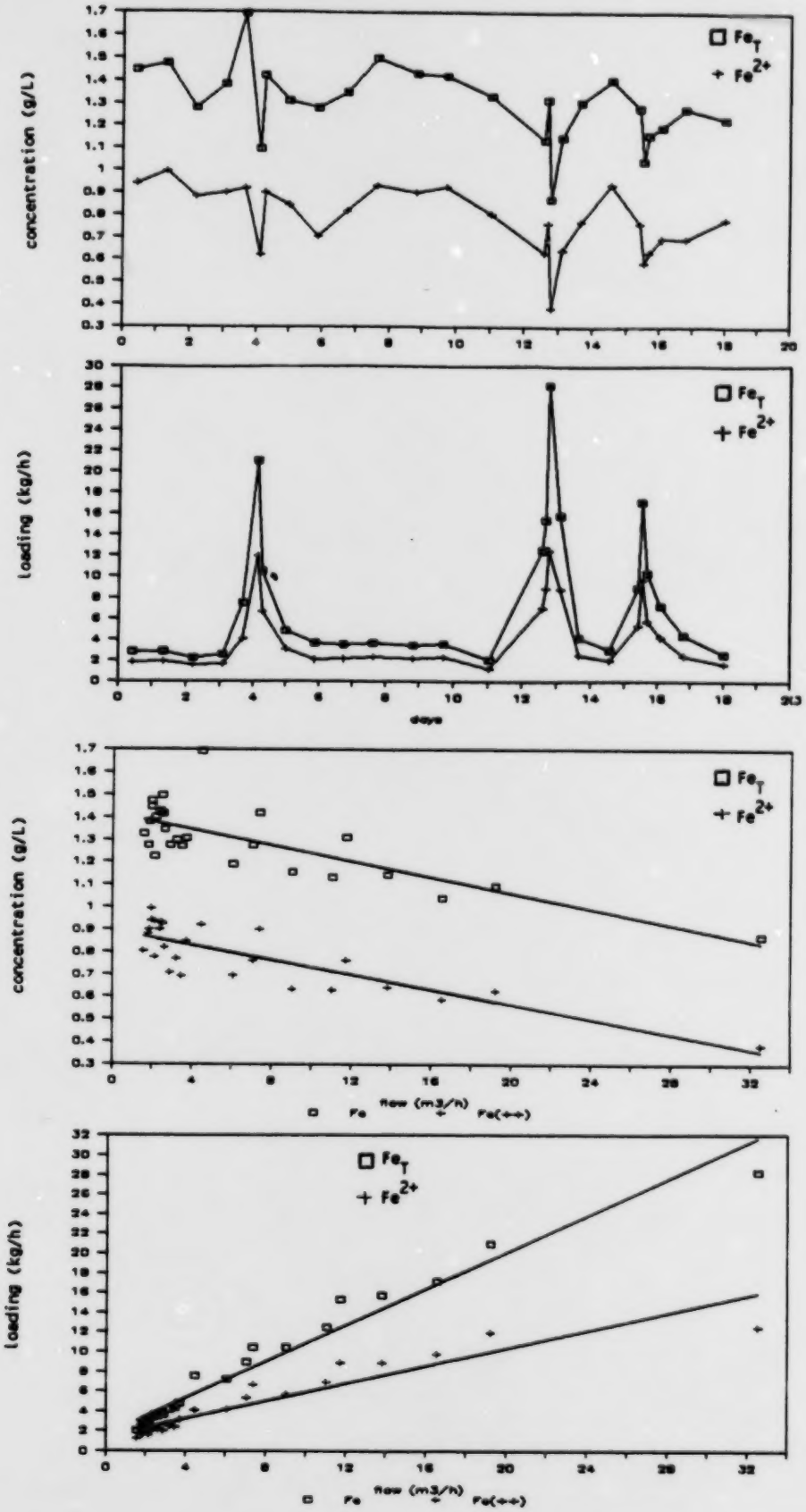


Figure 6 - Surface Flow, Iron Analyses and Loading at Station 2, Waite Amulet, 16 September to 6 October 1987

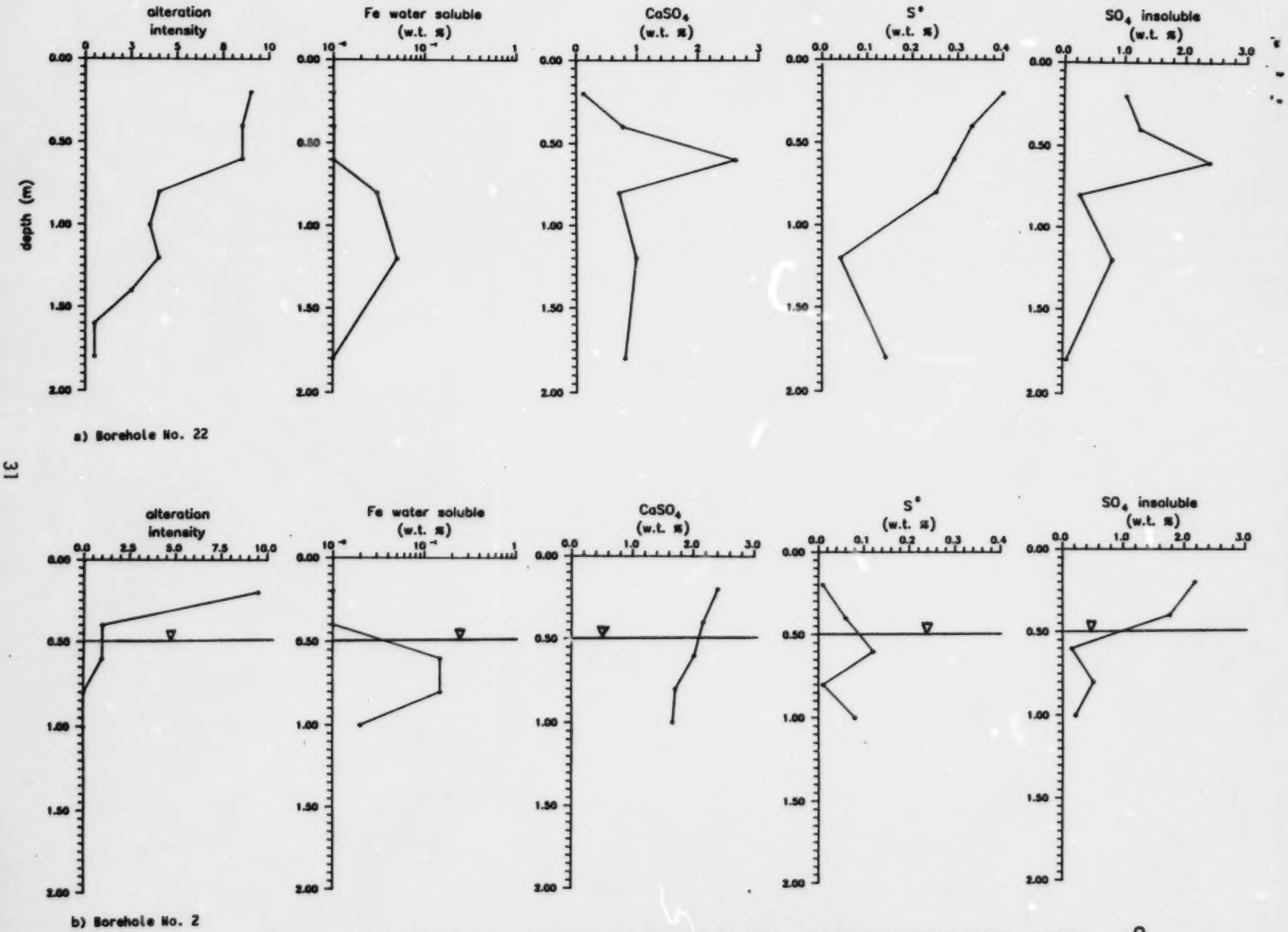


Figure 7 - Variation in Alteration Intensity, Water Soluble Fe, $CaSO_4$, S^o, and Insoluble SO_4 for Cores from Piezometer Locations 2 and 22

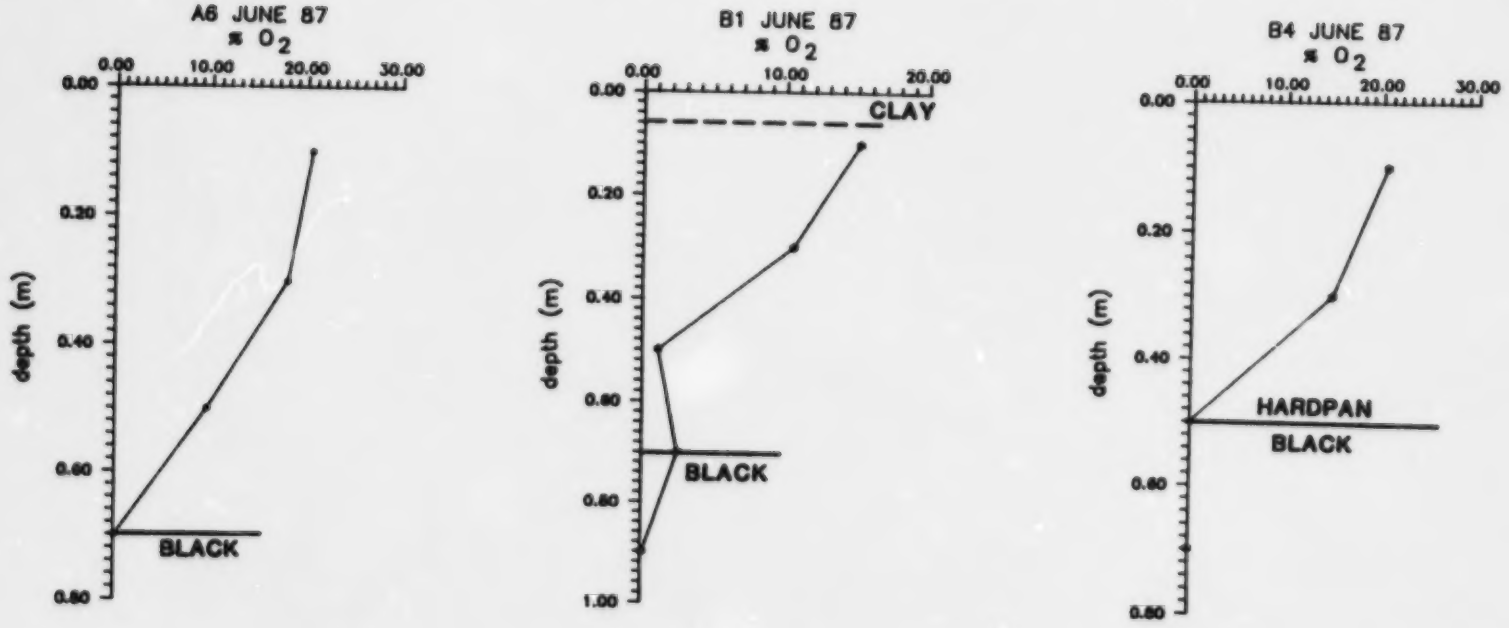
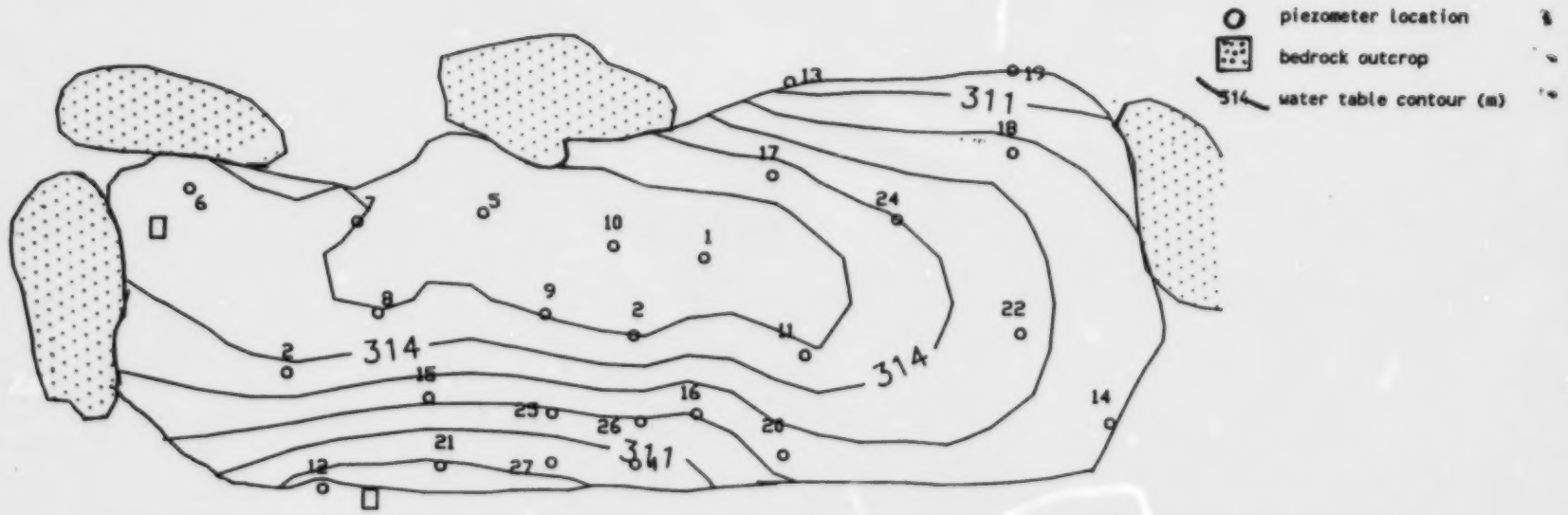


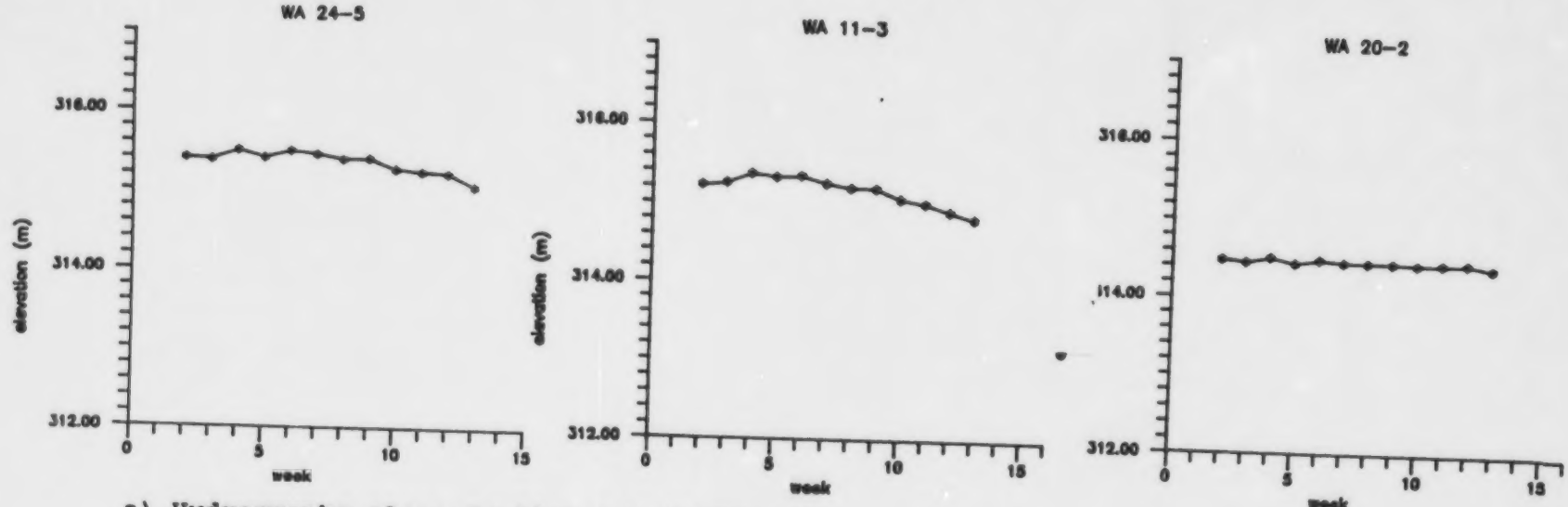
Figure 8 - Oxygen Profiles for Waite Amulet a) Without Hardpan; b) With Hardpan; and c) With Clay Cover



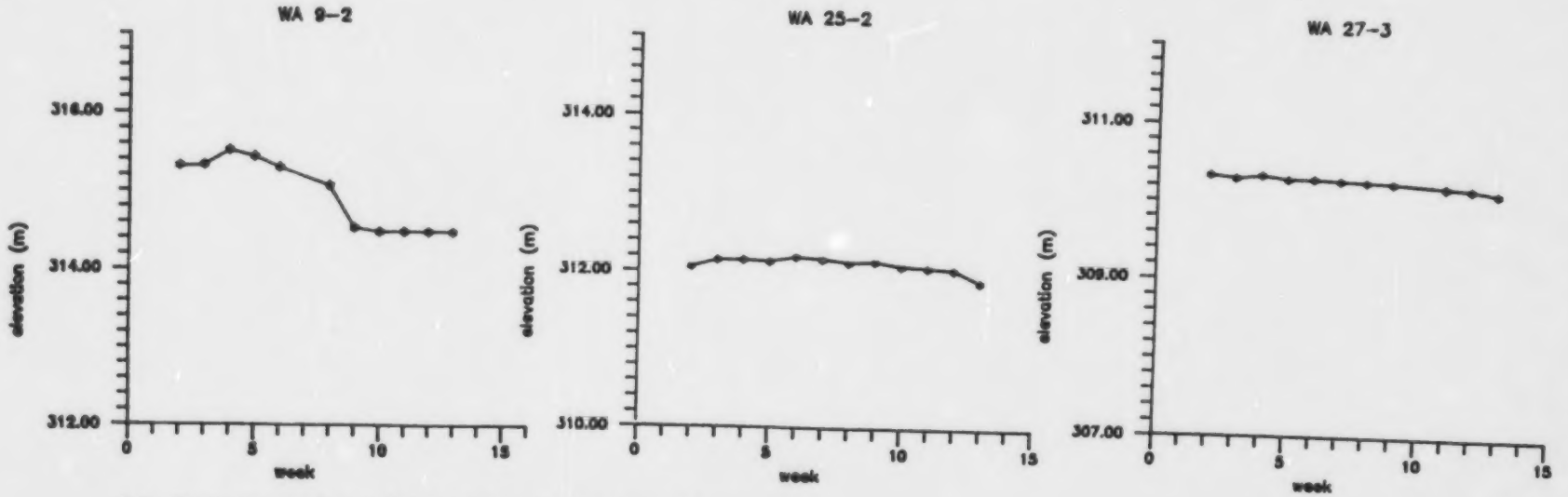
a) Water table, 18 May 1987

b) Water table, 11 August 1987

Figure 9 - Water Table Configurations for May and August 1987



a) Hydrographs along Section A-A (Figure 9)



b) Hydrographs along Section B-B (Figure 9)

Figure 10 - Hydrographs for Piezometers Along Section A-A and B-B, 18 May to 11 August 1987

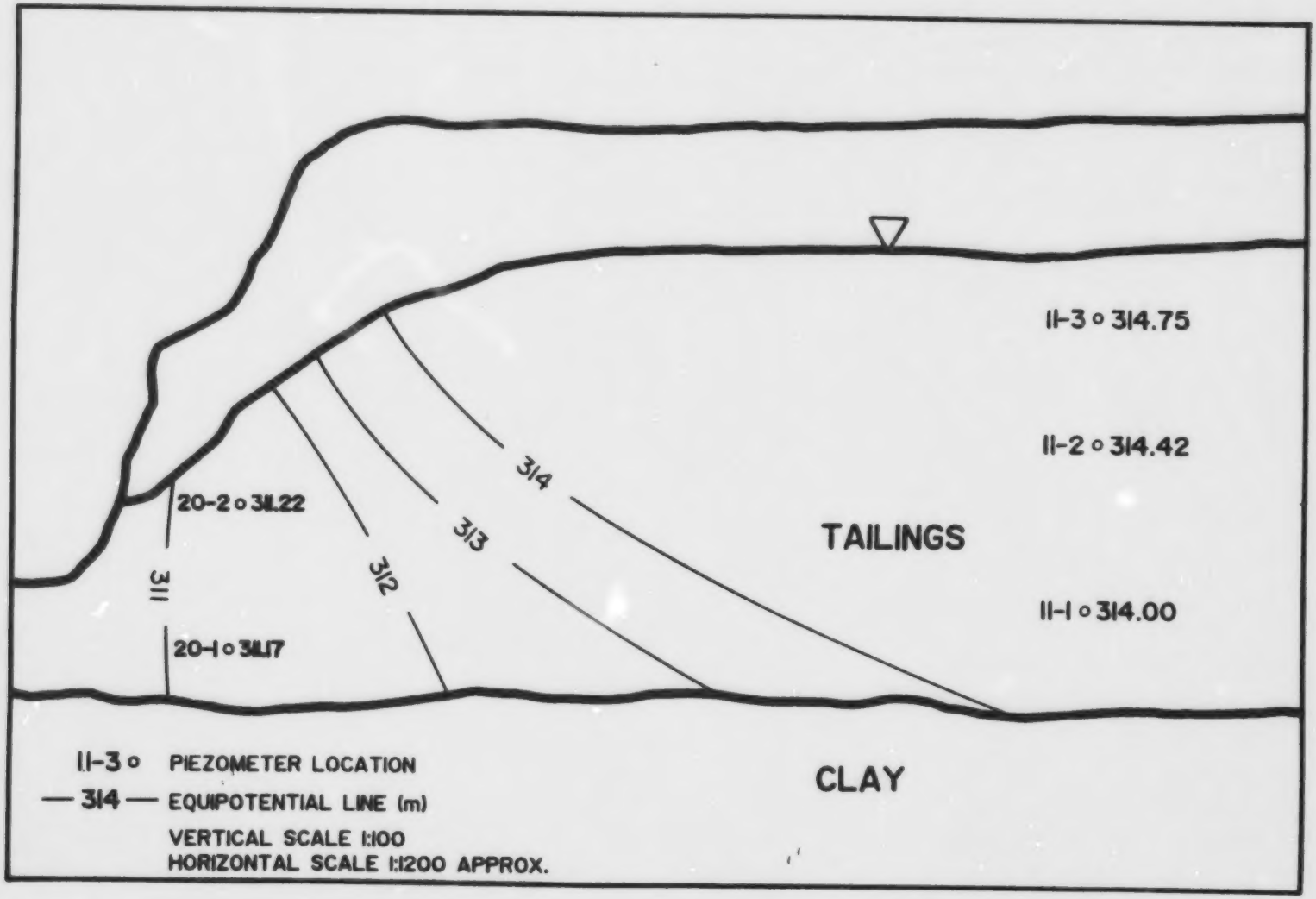


Figure 11 - Approximate Equipotential Lines, Section A-A, August 1987, Waite Amulet

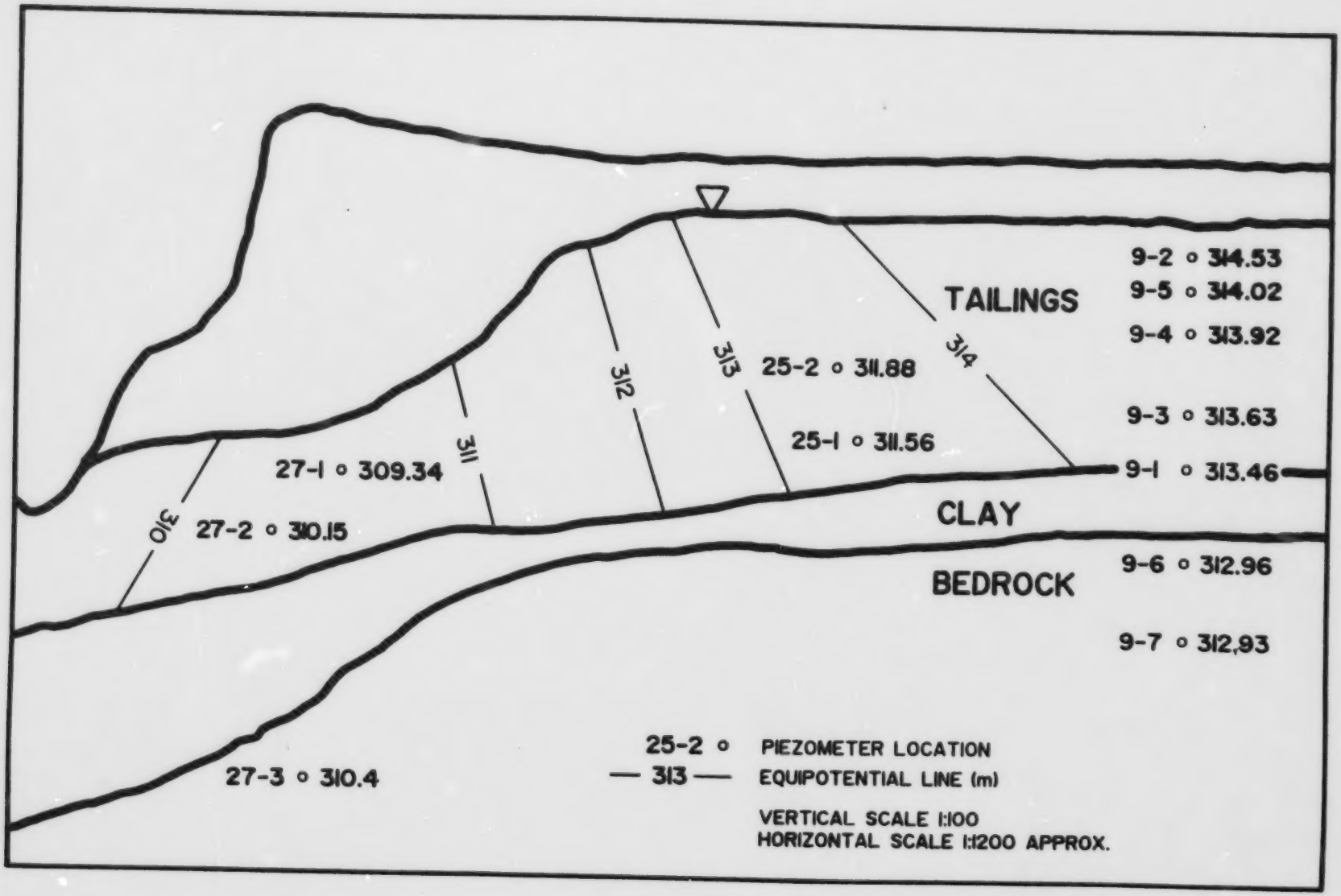


Figure 12 - Approximate Equipotential Lines, Section B-B, August 1987, Waite Amulet

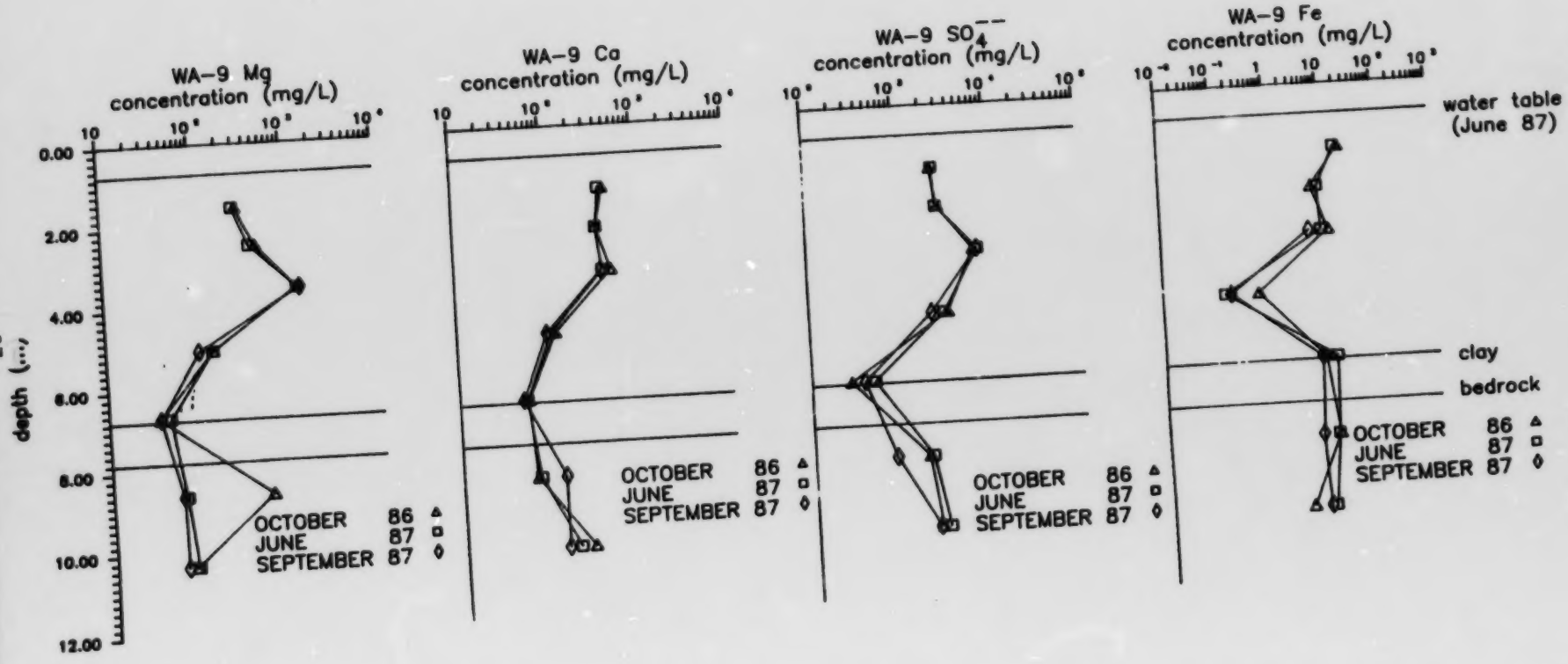


Figure 13 - Comparison of Results of Three Sampling Rounds for Station 9

Volume

2

RESEARCH REPORT

N-8523 : RR 88-1

HYDROGEOCHEMICAL INVESTIGATION OF REACTIVE TAILINGS AT WAITE AMULET TAILINGS SITE, NORANDA, QUEBEC - PHASE 3 - 1987 PROGRAM

VOLUME II - APPENDICES

Final Report by
R. Siwik, L. St-Arnaud, R. Prairie, L. Labrosse
March 1988

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KEYWORDS

Acid Mine Drainage
Acid Generation
Hydrogeology
Geochemistry
Mine Closure
RATS
Sulphides
Tailings
Waite Amulet

VOLUME II - APPENDICES

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- June 1987
- September 1987

APPENDIX A

STATEMENT OF WORK - HYDROGEOCHEMICAL INVESTIGATION OF REACTIVE TAILINGS AT WAITE AMULET TAILINGS, NORANDA, QUEBEC - PHASE III (1987)

1 Objectives

1.1. General Objectives

The overall objective of the RATS program is to eliminate the need for perpetual maintenance and water treatment for reactive tailings areas and waste rock. Achievement of this objective will require the development of a better understanding of the biohydrogeochemical process and controlling mechanisms. Based on this understanding, improved long-term tailings management practices can be developed.

1.2 Specific Phase 3 Objectives

The third year of the five-year study field program will:

- Evaluate the hydrogeochemistry of the tailings site including a water and metal balance.
- Evaluate gaseous O_2 profiles under clay-covered, directly-vegetated and untreated sites.
- Assess oxidation control options for field trials.

2 Scope

2.1 Evalulate Hydrogeochemistry

The 1987 field program will provide a baseline monitoring of total metal loadings and flow for the Waite Amulet tailing site. The precipitation and evaporation will be monitored and the data logged by equipment installed in May-June under the Phase 2 project.

Pore water movement and geochemistry will be evaluated using the 73 installed piezometers. The piezometers will be sampled twice during the 1987 field season. Field analysis will consist of pH, Eh, Ec, temperature and acidity. The samples will be preserved for subsequent analysis of Fe^{2+}, Fe Total, SO_4^{2-} and, possibly, Mg, Ca and Na at the Horne Division Environmental Laboratory. The 73 piezometers will be measured weekly or bi-weekly to monitor the water table fluctuation with rainfall events.

The western seepage face will be monitored for flow and quality using a flume and automatic sampler with data logger. Overland flow at the northern section of tailings will be monitored for flow and quality using a flume and automatic sampler with a data logger. The automatic samplers will be calibrated to flow and checked daily. The samples which are field preserved will be submitted to the Horne Division Environmental Laboratory for analysis of Fe^{2+}, Fe_T and SO_4.

The four suction lysimeters installed during the 1986 field season will be sampled to assess their effectiveness in sampling the unsaturated zone. It will then be decided whether and where the remaining eight lysimeters should be installed.

This data acquisition program will continue for a three-year period (1987-1989). Factors affecting the water quality and flow through a tailings dam will then be more clearly understood.

2.2. Evaluate Gaseous O_2 Profiles

A more complete survey of gaseous O_2 profiles will be conducted on the Waite Amulet site to assess the gaseous O_2 diffusion into the tailings. A grid pattern will be established over the forty hectare tailings site and O_2 will be monitored with depth. A core sample will also be taken to measure the visual depth of oxidation, for moisture content and grain size distribution. This is an extensive survey and is expected to be completed during a four month period with the aid of a summer student.

2.3 Relate Mineralogy to Pore water Geochemistry

Based on the existing data, Noranda Research Centre will correlate in consultation with the client (CANMET) and the sub-contractor (University of Waterloo) the unsaturated zone pore water geochemistry, O_2 profiles and mineralogy.

2.4 Assess Oxidation Control Options

Via a separate project, laboratory methods (8) for evaluating dry barriers for oxidation control are being developed. Field trials of the options under consideration will be scoped. (Note that funds for conducting such field tests have not been allowed for in this project).

Phase 3 (1987) - Hydrogeochemistry of Waite Amulet

	1987-1988										
	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Total
Monitor piezometers water levels	——	——	——	——							1
Conduct O_2 profiles	——	——	——	——							4
Evaluate mineralogy and geochemistry	——	——	——	——	——	——					10
Sample piezometers		——			——						30
Monitor seepage and over land flow	——	——	——	——							20
Data processing	——	——	——	——	——	——	——	——	——	——	5
Project management	——	——	——	——	——	——	——	——	——	——	5
Planned			20.0	7.0	15.0	10.0	5.0	5.0	5.0	8.0	75.0

Costs are reported in $1,000
Project cost shared $35 k by Noranda, $40 k by DSS

Figure A-1 - Project Schedule and Cash Flow

APPENDIX B

CHARACTER AND DEPTH OF OXIDATION OF THE REACTIVE TAILINGS AT THE WAITE AMULET MINE SITE, NORANDA, QUEBEC (J.L. Jambor, Process Mineralogy Section, Mineral Processing Laboratory, CANMET, July 1987)

Energy, Mines and Resources Canada
Energie, Mines et Ressources Canada

CANMET
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

CHARACTER AND DEPTH OF OXIDATION OF THE REACTIVE ACID TAILINGS AT THE WAITE AMULET MINESITE, NORANDA, QUEBEC

J.L. Jambor
Process Mineralogy Section
Mineral Processing Laboratory

July 1987

Project: 30.86.02
Tailings Management

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 87-97 (IR)

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CHARACTER AND DEPTH OF OXIDATION OF THE REACTIVE ACID TAILINGS AT THE WAITE AMULET MINESITE, NORANDA, QUEBEC

by

J.L. Jambor

ABSTRACT

Microscopic examination of 82 polished sections from 69 core samples of the Waite Amulet tailings pile has shown that alteration intensity consistently decreases with increasing depth. The near-surface zone is strongly oxidized, as is indicated by the destruction of almost all pyrite and pyrrhotite, but the relative immaturity of gossan development is evident from the absence of a significant leached zone, the retention of iron oxyhydroxides as pseudomorphs of sulphides, and the lack of hardpan in the core samples. Iron released from the oxidation of sulphides is incorporated mainly in goethite, lepidocrocite, ferrihydrite, and jarosite, whereas sulphate is precipitated mainly as gypsum crystals and jarosite. Beneath the upper oxidized part of the tailings is an intermediate zone of weak alteration which is succeeded downward by a zone of negligible sulphide alteration. Gypsum occurs throughout the tailings pile, but is generally most abundant in, and near, strongly oxidized material. Iron in the water-soluble fraction of the tailings typically is concentrated in the upper part of the intermediate zone, and jarosite abundance closely follows the vertical profiles for microscopically determined alteration intensity.

Keywords: tailings, sulphides, alteration, oxidation, depth profiles, Waite Amulet, Quebec.

CARACTÈRE ET INTENSITÉ DE L'OXYDATION DES RÉSIDUS ACIDES RÉACTIFS QUI SE TROUVENT SUR L'EMPLACEMENT DE LA MINE WAITE AMULET, À NORANDA (QUÉBEC)

par

J.L. Jambor

RÉSUMÉ

Un examen microscopique de 82 sections polies de 69 échantillons carottés provenant de l'amas de résidus sur l'emplacement de Waite Amulet a révélé que l'intensité de l'altération diminue en fonction de la profondeur. La destruction de la plus grande partie de la pyrite et de la pyrrhotite dans la zone près de la surface révèle que celle-ci est fortement oxydée. Cependant, l'absence d'une zone de lessivage importante, la rétention d'oxydes de fer hydratés comme pseudomorphes des minéraux sulfurés et l'absence de cuirasse ferrugineuse que dénotent les échantillons carottés indiquent que le développement du chapeau ferrugineux est relativement prématuré. Le fer libéré par l'oxydation des sulfates est incorporé principalement dans la goéthite, lépidocrocite, ferrihydrite et jarosite tandis que le sulfate est en grande partie précipité sous forme de cristaux de gypse et de jarosite. Au-dessous de la couche oxydée supérieure de résidus se trouve une zone intermédiaire faiblement altérée suivie d'une zone qui a été très peu altérée par les sulfates. Le gypse est présent dans tout l'amas de résidus, mais se retrouve en plus grande quantité dans les matériaux fortement oxydés ou à proximité de ceux-ci. Le fer contenu dans la fraction des résidus qui est soluble dans l'eau est concentré d'une manière typique dans la partie supérieure de la zone intermédiaire. L'abondance de la jarosite suit de près les profils verticaux de l'intensité de l'altération qui ont été déterminés au microscope.

INTRODUCTION

The Waite Amulet minesite near Noranda, Quebec (Fig. 1) contains about 5.9 million tonnes of sulphide-rich tailings in an elevated 41 hectare dam. The tailings are 2 to 15 m thick, and were accumulated as the wastes from 10 orebodies mined during the interval 1929-1962. The tailings and site are undergoing detailed hydrogeochemical studies as part of the RATS program (Reactive Acid Tailings Study). Noranda Research Centre and CANMET are joint participants in the Waite Amulet study.

As part of the Waite Amulet investigation, nine holes were cored through the tailings pile in 1985. Core samples from hole WA-20 were examined mineralogically by Petruk and Pinard (1986), and their image analysis study provided quantitative abundances of the tailings minerals and alteration products that occur in one vertical section through the tailings pile. Because the alteration products are complex and extremely fine-grained mixtures that are difficult to identify as specific mineral phases, a detailed mineralogical study of core WA-20 also was done by Jambor (1986), who used mainly optical microscopy and X-ray powder-diffraction methods to characterize the phases. As well, chemical analyses of bulk samples were used to estimate the abundances of specific alteration minerals that had been identified by the microscopic and X-ray techniques.

Hole WA-20 is located on a bench along the western side of the tailings pile (Fig. 1,4) and therefore is not representative of the hydrogeological environment that applies to the bulk of the pile. To obtain a better indication of the character of the tailings existing in saturated conditions, an additional 31 core samples selected from piezometric sites were examined

mineralogically and chemically (Jambor 1987). The study showed the cores to be unaltered, as was indicated by the negligible amounts of altered sulphides. As a consequence of these earlier studies, it was concluded that microscopic examination of polished sections of the tailings is, by itself, a viable method of discriminating between altered and unaltered samples. Therefore, the need for chemical analyses of tailings samples that are in an observably pristine, unaltered condition, can be reduced substantially. On this basis, to further evaluate mineralogical conditions in the near-surface, unsaturated zone, it was agreed that an additional 72 core samples would be examined in polished section to establish the relative degree of alteration in each sample; the assumption was that a significant number of samples would be in a relatively unaltered state. The identification of pristine samples is in itself extremely useful information, but the immediate, practical concern was the need to reduce the number of samples that would require more thorough mineralogical and chemical studies.

SAMPLES AND SAMPLE SITES

The core samples are from 6 holes which, together with WA-20, represent two vertical cross-sections approximately along the length and width of the tailings pile (Fig. 2). The number of cores from each hole ranged from 6 (hole WA-2) to 18 (hole WA-1). As in the study of the cores from the piezometric sites (Jambor 1987), the as-received cores were wrapped in labelled plastic bags and the cores were in a frozen state. The samples were stored in a freezer at CANMET until the thawing and drying operations began.

The as-received samples consisted of half of the original core and aluminum core barrel, the split having been achieved by lengthwise band-saw

cutting of the frozen core and encapsulating barrel. On each barrel was marked the borehole and sample numbers, and the upward (toward surface) direction was indicated by an arrow.

SAMPLE PREPARATION

The frozen core was separated from its aluminum casing, which was discarded, and each core was placed in a separate, labelled white box and allowed to thaw at room temperature. The colour of the boxes proved to be important as an evidently sensitive indicator of acidic reaction from the excess moisture in the cores. Care also was taken to orient the cores in a consistent downhole direction, thereby ensuring that the observed oxidation profiles were placed in their appropriate positions.

The room-temperature drying, sieving, and blending of each core sample followed the procedures outlined previously (Jambor 1986) and need not be repeated in detail. As before, the tailings were screened to minus 36 mesh (aperture size 425 micrometres) and various splits and reference samples were selected before and after screening. Prior to screening, a few of the cores were partitioned into sub-samples that preserved special features; for example, where part of a core consisted of ocherous, strongly oxidized tailings in relatively sharp contact with black, sulphide-rich core, an effort was made to divide the core into two representative fractions.

In order to minimize the dissolution of water-soluble phases, all of the polished sections were prepared using non-aqueous media. For the polished sections, the -36 mesh samples were rescreened to -270 mesh (aperture size 53 micrometres) and the fines were rejected. Although 72 cores were received

initially, 3 of the organic-bearing, clay-rich surface samples were not examined in polished sections. Because of the sub-sampling of some cores, however, 82 polished sections were prepared from the remaining 69 cores, and 81 separate samples were available for chemical analyses.

Contamination

Except for the removal of large, coherent pieces of organic material such as pine needles and well-preserved twigs, the standard procedure in sample preparation was to crush and screen the complete sample or sub-sample (excluding small portions which were retained as coarse reference material). Two samples from hole WA-8 were treated differently, however, because they contained an obvious contamination that was removed readily. These samples, C-5 and C-6, consist of black, sulphide-rich tailings beneath the strongly oxidized, ocherous, near-surface cap. The C-5 and C-6 sulphide-rich cores each contained a thin rim of ocherous material only at the interface of the core barrel and main core, thereby indicating that the ocherous rind was a contaminant from the up-hole, oxidized zone. The contaminant was removed from the frozen core by using a water spray. Only in these two cores was the contamination so pronounced and so accessible, and no other cores were treated in this manner.

Acid losses

As was done in the study of the cores from the piezometric sites (Jambor 1987), the thawing and initial drying of the cores occurred in shallow boxes of thin, white cardboard. Only with the present series of samples was a reaction with the cardboard observed: for several samples the moist base of the box eventually turned brown, whereas other samples showed no effect. The browning of the cardboard indicates that an acidic reaction had occurred, and

thus there was some loss of water-soluble sulphate. That the sulphate losses were probably small was inferred from the absence of visible precipitates. Nevertheless, as a check the remaining halves of cores C-8, C-9, and C-10 (hole WA-8), which had been retained in a frozen state at Noranda Research Centre, were again sawn in half and a split of each was shipped to CANMET. One split of each sample, comprising one-quarter of the original core, was received in a frozen state and was air-dried and sieved in the normal manner, except that the drying was done in plastic-lined trays. Table 1 lists all of the cores from which the acidic, browning effects were observed, and Table 2 gives a comparison of the soluble-sulphate results obtained for cores WA-8, C-8 to C-10. Unfortunately, the 3 sets of samples do not show a consistent trend: in 2 of the pairs (C-9 and C-10), increases in pH but losses of some sulphate are indicated. In contrast, in the C-8 pair the pH and analytical SO_4 are higher in the original sample than in the quarter split. New analyses of the C-8 sample, done in duplicate, confirmed the high sulphate obtained in the original analysis. Consequently, although no definitive conclusions can be made, it seems likely that the amount of acid lost in the original drying procedure was not appreciable.

MEGASCOPIC CHARACTER OF CORES

Unlike the cores from the piezometric sites, the samples from each borehole in the present series include a well-defined oxidized zone near the beginning of the sample sequence (Fig. 5). The initial sample (C-1) from each hole also contains clay, soil, or abundant organic matter, and it thus is assumed that the consecutively numbered sample sequence for each hole represents a vertical profile from surface to progressively increasing, but unspecified depths.

Although none of the cores from the piezometric sites contained strongly oxidized zones, a few thin, weakly oxidized "iron-stained" layers were noted to occur erratically. These weakly oxidized layers were interpreted to be minor paleosurfaces at which local oxidation occurred during interruptions in the accumulation of the tailings pile. The same type of local oxidation is present in a few of the current series of cores, but the paleosurface origin of the alteration is clearly evident from the concentrations of vegetation in, or at the contacts, of some of the oxidized layers.

Table 3 summarizes the general megascopic features of the cores from each drillhole. Each of the holes shows a strongly oxidized, sulphide-depleted near-surface zone which progresses downward to a sulphide-rich zone. Colour is a good indicator of this progression, the change being from shades of yellow or brownish yellow, to black. Also evident in Table 3 is that the clay-rich surface samples intersected in holes WA-8 and WA-1 are carbonate-rich, a feature which presumably is the manifestation of lime addition to the tailings surface. By contrast, surface or near-surface cores that lack a clay-rich zone do not contain carbonates. Regardless of whether a lime-rich surface is present or absent, the strongly oxidized upper parts of all holes contain abundant crystals of gypsum that occur as clear, disseminated euhedra, typically 0.5 to 1.0 mm long.

In addition to the gypsum euhedra, whose size and quantity indicate in-situ crystallization in the tailings, small amounts of sulphates were deposited from the aqueous phase contained in the as-received cores. These precipitates consist of fine-grained, fibrous, radiating aggregates of gypsum (Fig. 6), and more-copious ferrohexahydrite, $FeSO_4.6H_2O$. The latter forms sparse white blooms that consist of thin coatings, beads, and filiform aggregates on sulphide-rich samples (Fig. 7).

MICROSCOPIC CHARACTERIZATION

Alteration of the Waite Amulet tailings is generally intense near surface, but this intensity nevertheless is only at moderate levels relative to alteration features that typify a completely mature gossan. For example, although only traces of relict sulphides occur in the uppermost, near-surface zone, the almost invariable presence of these sulphides, especially chalcopyrite, is an indication of the incompleteness of the oxidizing and leaching processes. The lack of maturity also is manifested not only by the shallowness of the interval over which appreciable sulphide oxidation has occurred, but also by the preservation of abundant magnetite grains throughout the oxidized portion of the tailings.

Alteration intensity of the Waite Amulet tailings has been classified on a scale of 0 to 10. The purpose of the introductory remarks above is to emphasize that a rating of 10 does not signify that oxidation is virtually complete; the value is only a relative measure, and in the present scheme a 10 rating indicates that pyrrhotite and pyrite have been obliterated and only traces of sulphide, typically chalcopyrite, remain. A rating of 9 indicates that a few grains of pyrite are observable in an otherwise sulphide-purged oxidized sample. The appearance of vestiges of pyrrhotite would lower the alteration rating to an 8 or 7, the value depending on the number of remnants observed and their degree of preservation. Values below 7 are in essence measures of the intensity of pyrrhotite alteration; this alteration is reflected both by textures (e.g., residual sulphide cores versus only narrow alteration rims), and by the proportions of pyrrhotite grains affected to one degree or another.

The following comments briefly summarize the features observed in polished sections. Additional data are given in Table 4, and Figures 8 and 9 consist of cross-sections illustrating the variations in alteration intensity with depth in each borehole.

Hole WA-2

Six polished sections of core from borehole WA-2 were examined microscopically. The upper part of the hole is strongly oxidized, and the change to relatively unaltered material is sharply demarcated in core sample C-2. Indications of a weakly copper-enriched supergene zone are present in sample C-5.

Hole WA-8

Nine polished sections were examined. A peculiar feature is that all deeper samples consist of material that falls in the very fine-grained category (Table 4). Weak alteration extends to greater depths than that in WA-2, but otherwise the alteration profiles of the two holes are similar (Fig. 8). The magnetite content in WA-8 is noticeably lower than that of other holes.

Hole WA-11

Twenty polished sections were examined. As in the preceding holes (WA-2, WA-8) the uppermost samples are strongly oxidized and the downward progression is to negligible alteration. In WA-11, however, a second strongly oxidized zone appears at sample C-6 (Fig. 8). This thin zone is interpreted to be an oxidized paleosurface, probably continuous with similar zones noted in holes WA-1 and WA-17 (Table 3).

Hole WA-22

The eleven polished sections examined show the normal trend of decreasing alteration intensity with increasing depth, but the change is more gradual than in other holes (Fig. 8). The uppermost, strongly oxidized zone is typically almost devoid of sulphides, and traces of covellite appear at the bottom of this zone (sample C-3B). Marcasite was observed in three of the polished sections in the weakly altered zone, and this mineral also was noted to occur in the weakly to negligibly altered parts of holes WA-8 and WA-11.

Hole WA-17

Nearly all of the 15 polished sections examined consist of coarse-grained material (Table 4). The strongly oxidized zone near surface is rather shallow (Fig. 9) and the underlying samples (C-2,3,4) contain traces of covellite. Samples C-6 and C-7 include material from moderately oxidized paleosurfaces. The alteration intensity of samples in the moderately oxidized zone is difficult to rate numerically because most samples contain a relatively high proportion of unaltered pyrrhotite.

Hole WA-1

As in WA-17, nearly all of the 18 samples examined from hole WA-1 consist of coarse-grained material. The strongly oxidized zone is relatively thick and is fairly well demarcated, and a zone of paleosurface oxidation is present at sample positions C-8 and C-9 (Fig. 9).

Hole WA-20

Polished sections from the 10 sample sites in hole WA-20 (Jambor 1986) were re-examined in order to obtain comparable ratings for the alteration intensity. All of the samples fall within the coarse-grained textural

category. The interruption in the trend of colour change previously noted at sample C-6 (Table 2 in Jambor 1986) may reflect the presence of a paleosurface at this position. The overall alteration profile for hole WA-20 is similar to that of WA-17 (Fig. 9).

Summary

The megascopic and microscopic observations have revealed a few patterns that were not evident in previous studies. The downward progression from an oxidized, sulphide-depleted zone near surface to an unaltered zone at depth is obvious, but additional much more subtle variations are present. Firstly, the cores from the northern end of the tailings pile (WA-2 and WA-8 in Fig. 2) are consistently much finer grained than those from the remainder of the pile. The boundary between the finer and coarser grained areas lies between hole WA-8 and the east-west cross-section (WA-17 to WA-20 in Fig. 2). Secondly, the east-west boundary also seems to mark the limit and approximate strike of a conspicuously oxidized paleosurface that is readily identified in at least 3 of the 4 holes in the section (Fig. 9). Thirdly, the two holes which yielded the finer grained material (WA-2 and WA-8) not only have the thinnest zones of strong oxidation, but they also lack a zone of moderate alteration (compare, for example, the profiles for holes WA-2 and WA-8 versus WA-22, WA-17, WA-1, and WA-20). The difference may be related to grain size, with less oxidant penetration occurring in the finer grained material, but a more likely control is restricted oxidation because of the higher water table at WA-2 and WA-8 (Fig. 3). The difference, however, also could be related to minor oxidation that occurred during the accumulation of the tailings pile. The inference is that holes WA-2 and WA-8 are sited in an area where the most recent deposition of tailings occurred, but the validity of this inferred chronological (stratigraphic) sequence is not known to the writer. Fourthly,

covellite had not been detected previously but was observed in 11 of the samples from the current suite. Only 1 of the occurrences is in the near-surface strongly oxidized zone, but 9 of the 11 are in the underlying zones of moderate alteration. Lastly, the distribution of marcasite is similar to that noted in hole WA-20 (Jambor 1986). Thus the oxidation profiles again can be broadly generalized into (a) a sulphide-depleted, strongly oxidized near-surface zone; (b) an intermediate zone in which only moderate to weak alteration has occurred, and marcasite has formed by replacement of pyrrhotite; (c) an unaltered zone at depth where the tailings are in a relatively pristine state.

CHEMICAL ANALYSES

The previous studies of Waite Amulet cores showed that combined megascopic and microscopic studies provide a reliable measure of the state of alteration of the tailings, and that specific chemical analyses can be used to quantify the abundances of some of the various alteration minerals (Jambor 1987). Because of the large number of samples available for the present study, and the impracticality of chemically analyzing all of them, the megascopic-microscopic observations were used as a guide to reduce the number of samples for analysis. Nearly all of the samples selected for deletion were from the water-saturated zone. Because some of the individual cores had been split into sub-samples, however, and because of the desire to maintain not-too-distant intervals even in the water-saturated zone, the result was that 50 samples were analyzed. As in the previous studies the interpretations, supported by the mineralogical studies, are that the water-soluble fraction of the tailings contains the $FeSO_4.nH_2O$ and $CaSO_4.nH_2O$ minerals,

that the analyses for elemental sulphur reflect the presence of native sulphur, and that the sulphate fraction which is not water-soluble is bound in jarosite.

Table 5 lists the results of the chemical analyses, and also the calculated amounts of SO_4 required to use up all of the Ca and Fe in the water-soluble fraction. Additional SO_4 not required by the Ca and Fe compounds is tabulated as Remnant SO_4. The final column in Table 5 gives the value obtained by subtraction of the wt. % water-soluble sulphate from that of total sulphate; the value is in essence a measure of the amount of jarosite present in each sample because jarosite is the only less-soluble sulphate mineral known to occur in the tailings, and its presence in relatively copious amounts is readily verifiable.

pH results

The pH values in Table 5 represent determinations done on the unfiltered sample-water suspensions used for the analyses of the water-soluble constituents. The pH values range from 8.0 to 3.3, but systematic trends are evident. The two highest pH values (8.0 and 6.3 in samples WA-8, C-2 and C-3) are from near-surface material to which there presumably has been addition of agricultural limestone: both core samples are carbonate-rich and have been confirmed by X-ray diffraction to contain calcite. Except for these 2 samples, the pH range is 5.8 to 3.3; the trend from low pH values in the upper oxidized zone to higher values in the unaltered tailings at depth is well defined (Fig. 10, 11).

Water-soluble constituents

The Fe contents of the water-soluble fraction average less than 0.03 wt. %. The highest value, 0.23 wt. %, is from sample WA-11, C-3, which has been

confirmed to contain siderotil, $FeSO_4.5H_2O$. The cross-section profiles (Fig. 12, 13) show clear indications that water-soluble iron is depleted in the strongly oxidized zone and accumulates or is generated in the underlying zone of moderate oxidation.

$CaSO_4$ variations are shown in Figures 14 and 15. The highest values generally occur in the strongly oxidized zone and in the upper, adjoining part of the moderately oxidized zone. The uppermost samples in holes WA-8, WA-11 and WA-2 (Fig. 15) are low in gypsum and are at the vegetation-rich surface of the tailings.

Remnant SO_4

Soluble sulphate not attributable to $CaSO_4$ or $FeSO_4$ is generally low, but exceeds 0.3 wt. % in 10 samples (Table 5). The anomalously high values have two distinct distributions, with roughly half of the high values occurring at the break between the strongly and moderately oxidized zones (i.e., roughly at the depth of the C-3 sample positions). The remaining half of the high values is from samples in hole WA-8, but these samples are not altered significantly. Previous attempts to identify a cation that is bound with the remnant SO_4 were unsuccessful (Jambor 1987), and no appropriate water-soluble sulphate has been observed in the present study. In strongly oxidized material, however, sulphate-bearing ferrihydrite is present (Table 6). All of the ferrihydrite is poorly crystalline and gel-like, and presumably part of the absorbed sulphate is water-soluble. In the reverse process, expulsion of absorbed water is evident from the "mud crack" structure (Fig. 21) that develops as a result of desiccation during room-temperature drying.

Elemental sulphur

The distribution profiles for elemental sulphur are shown in Figures 16 and 17. The highest sulphur values generally occur toward the base of the strongly oxidized zone. Excluding previously studied hole WA-20, and the three highest values in the present study, the remaining 47 samples average 0.16 wt. % S. Of the aforementioned three highest values, two are from jarosite-rich samples; the other sample, however, is not especially rich in jarosite but the presence of native sulphur could not be confirmed.

Insoluble sulphate

The last column in Table 5 represents the sulphate that is not readily soluble in water, and in essence the values are a measure of jarosite content. The correlation between observed jarosite occurrences and the chemical data is excellent, and the oxidation profiles (Fig. 18, 19) show that alteration intensity and insoluble sulphate have remarkably similar trends.

MINERALOGICAL OBSERVATIONS

The initial mineralogical study of the Waite Amulet tailings (Jambor 1986) focused specifically on the identification of the minerals that make up the fine-grained, complex alteration products. The subsequent studies (Jambor 1987, and this work) have had a broader, less focused chemical-mineralogical approach. Nevertheless, the more recent studies have considerably expanded the mineralogical data base and have shown that some false impressions were obtained from the examination of core WA-20. For example, the water-soluble sulphate fraction from WA-20 was thought to have been derived largely from bassanite, $2CaSO_4.H_2O$, and it was thought that the calcium contribution might have been derived, or at least enhanced, by the

addition of lime to the tailings surface. The newer studies have shown that virtually all of the soluble calcium is present as gypsum, $CaSO_4.2H_2O$, that occurs as euhedral single crystals up to 1 mm long. These crystals are distinguished readily from the small amount of fine-grained gypsum that crystallizes from the solutions evaporated during drying of the as-received cores. The relative coarseness of the crystals, their uniform size, and their occurrence throughout the tailings (including the water-saturated zone) suggest that gypsum formation, rather than being related specifically to lime addition, is more likely a natural and integral part of the chemistry of the whole tailings system.

The present study also has given indications of what happens to the small amounts of copper and zinc in the tailings. Chalcopyrite is surprisingly resistant to dissolution in the oxidation zone; eventually however, the mineral is leached and part of the copper is precipitated as covellite, thus emulating supergene alteration. The remainder of the copper, plus that eventually contributed by the breakdown of covellite, is incorporated in trace amounts as a solid-solution element in sulphates. Most of the copper occurs in the water-soluble sulphates and thus is eventually flushed out of the system. Unlike copper, zinc from the breakdown of sphalerite remains in solution or is ephemerally precipitated only in the $(Fe,Zn,Cu)SO_4.nH_2O$ sulphates.

Iron derived from the oxidation of pyrite, pyrrhotite, and magnetite to a lesser extent, is precipitated locally in small amounts as the soluble iron sulphates $FeSO_4.nH_2O$. On dried cores the prevalent species is ferrohexahydrite ($FeSO_4.6H_2O$), but coexisting siderotil ($FeSO_4.5H_2O$) also has

been identified. On one sample minute amounts of an unidentified Ca-Fe sulphate occur as a bloom associated with ferrohexahydrite and gypsum (Fig. 22). It is probable that the monohydrate (szmolnokite), the tetrahydrate (rozenite) and the heptahydrate (melanterite) exist at the tailings site; the highest of these hydrates precipitates readily in a moist environment, and dehydration to the tetrahydrate occurs rapidly under natural conditions once the moisture source is removed.

The ferrous sulphates are quantitatively insignificant precipitates when compared with the amount of iron that has been deposited as jarosite and various iron hydroxides. Although the sulphides in the near-surface zone have been oxidized, that much of the iron has remained in situ is evident from the widespread occurrence of oxides pseudomorphous after sulphides. The destruction of sulphides, which have high densities, coupled with the retention of iron in the oxidized zone, indicates that this zone should show a net increase in Fe wt. %. To achieve the formation of hardpan, it would be necessary to have additional leaching to remove the near-surface iron so that it could be redeposited and concentrated as an interstitial binding agent.

The jarosite in the Waite Amulet tailings is normal potassium jarosite. Presumably the potassium is derived largely from the destruction of K-feldspar, but alteration of silicates has not been examined. The highest jarosite content is in sample WA-11, C-3ox (Table 5); the jarosite-rich layered material in this sample could be considered as a primitive stage in the development of hardpan.

In the previous studies the presence of both goethite and lepidocrocite (two forms of FeOOH) was confirmed by X-ray diffraction patterns. In the present study these minerals have been noted to co-exist on an intimate scale, i.e., as mixtures that have replaced individual grains of pyrrhotite. Additionally, the common presence of ferrihydrite, ideally $5Fe_2O_3.9H_2O$, has been recognized in the strongly oxidized zone (Fig. 21, Table 6). Ferrihydrite typically is disordered and gives poor X-ray diffraction patterns, but observations suggest that this mineral is widespread in small amounts. In the saturated zone, for example, what is either ferrihydrite or amorphous iron oxide-hydroxide appears as a glazed brownish coating on grain aggregates, but the glaze is too thin, or the crystallinity too poor, to obtain confirmation by X-ray diffraction. In the strongly oxidized zone, however, a few of the coatings are considerably thicker, and local concentration into sedimentary-type layers up to 1 mm thick have been observed.

Ferrihydrite is unstable with respect to goethite and hematite, and the transformation occurs in a variety of conditions (Torrent and Guzman 1982; Torrent et al. 1982). Lepidocrocite is metastable with respect to goethite, and it has been concluded that the formation of lepidocrocite involves the presence of Fe^{2+} as a necessary precursor (Schwertmann 1985). Silica evidently inhibits crystallization of goethite and lepidocrocite, thereby favouring the formation of ferrihydrite (Carlson and Schwertmann 1981 ; Cornell et al. 1987). Thus, it may be significant that the analyses of Waite Amulet ferrihydrite indicate the presence of small amounts of Si (Table 6), but the silica contents nevertheless are minor as compared to sulphate.

Recommendation for further studies

Two additional aspects of the Waite Amulet mineralogy merit additional study. Firstly, the alteration of silicate minerals has not been investigated and at this point it is only an assumption that the breakdown of K-feldspar in the strongly oxidized zone is the principal source of the potassium that is precipitated from solution as jarosite. Likewise, if gypsum precipitates have not derived their calcium from the surficial agricultural lime, then other silicate-consuming reactions must have occurred and should be identified. Secondly, a suite of oxidized samples and precipitates was collected by this writer at the Waite Amulet tailings site in July 1987. Mineralogical characterization of these specimens should be done; possibly the precipitates being formed by seepage from the tailings differ from those formed within the tailings pile.

Whole-rock chemical analyses of some of the tailings cores might prove to be useful in charting the mineralogical reactions that are manifested in the oxidation profiles. Chemical analyses for total sulphur would be a simple method of quantitatively demonstrating the extent of sulphide destruction in the strongly oxidized material; sulphide-sulphur values should correlate with the microscopically determined alteration intensity (Fig. 8,9). Finally, to obtain an estimate of the quantity of sulphides that are in the tailings pile, the previously studied samples from the piezometric sites are being examined by image analysis to obtain their pyrite and pyrrhotite contents; these values will give an indication of the amount of sulphides that are a potential source of acid drainage.

CONCLUSIONS

Microscopic studies and chemical analyses of the Waite Amulet tailings have shown consistent trends of alteration wherein a strongly oxidized, sulphide-depleted near-surface zone gives way to pristine unaltered tailings at depth. In most holes the strongly oxidized zone is underlain by a variable thickness of weak alteration (the intermediate zone); the intensity of alteration in the intermediate zone appears to be greatest along the edge of the tailings (e.g., in hole WA-20). In addition to these general trends, a thin zone of moderate alteration t[illegible]s approximately east-west across the tailings pile at intermediate depths and marks a zone of paleosurface oxidation.

In the strongly oxidized zone nearly all of the pyrrhotite and pyrite have been destroyed. The principal alteration products are oxyhydroxides (goethite, lepidocrocite and ferrihydrite) and sulphates (jarosite and gypsum). Chemical analyses indicate that jarosite abundance correlates well with the microscopically observed alteration intensity. For the water-soluble fraction of the tailings, pH values generally range from 5.8 to 3.3; the trend from low values in the upper oxidized zone to higher values in the unaltered tailings at depth is readily apparent. Water-soluble Fe is highest in the moderately oxidized zone, whereas the highest values for $CaSO_4$ generally occur in the strongly oxidized and adjacent moderately oxidized zones. Sulphate in the tailings has been derived from the oxidation of sulphides, and presumably the breakdown of K-feldspar has provided the potassium incorporated in the jarosite precipitates. Partial destruction of other silicates may have provided the calcium now present as extensive gypsum precipitates, but this aspect of alteration needs further study.

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Table 1. Core samples which showed an acid attack on container boxes after the drying process

Borehole and Sample Numbers	Character of Core Sample	Strength of Stain
WA-2, C-1:	upper half oxidized, lower half sulphide-rich	light browning
WA-8, C-4:	yellowish brown, strongly oxidized except for bottom 1cm	light browning
C-5:	sulphide-rich, black	moderate browning
C-6:	sulphide-rich, black	strong browning
C-7:	sulphide-rich, black	very strong
C-8:	sulphide-rich, black	dark brown*
C-9:	sulphide-rich, black	strong browning
C-10:	sulphide-rich, black	light browning
WA-11, C-9:	sulphide-rich, black	strong browning
C-11:	sulphide-rich, black	strong browning
C-13:	sulphide-rich, black	strong browning
C-15:	sulphide-rich, black	moderate browning
WA-22:	no staining observed	
WA-1, C-13 to C-18 inclusive	all are black, sulphide-rich	all showed strong browning
WA-17, C-5:	sulphide-rich, black	light browning
C-7:	top 2 cm moderately oxidized, remainder black	strong browning
C-9:	sulphide-rich, black	light browning
C-12:	sulphide-rich, black	light browning
C-13:	sulphide-rich, black	light browning
WA-20:	samples received after drying - - no data	

*darkest brown, most intense reaction of all samples

Table 2. Water-soluble sulphate in samples which showed acidity losses (Table 1) versus results from new samples.

Borehole Sample Nos.	Strength of Stain*	Chem. Anal., Wt.%				Calc. Distributions, Wt.%		
		ph	Fe	Ca	SO_4	SO_4 as $CaSO_4$	SO_4 as $FeSO_4$	Remnant SO_4
WA-8, C-8	dark brown	4.8	0.13	0.46	1.98	1.10	0.22	0.66
C-8Q	-	4.6	0.06	0.45	1.35	1.08	0.10	0.17
WA-8, C-9	strong browning	4.3	0.07	0.39	1.17	0.94	0.12	0.11
C-9Q	-	4.4	0.05	0.46	1.38	1.10	0.09	0.19
WA-8, C-10	light browning	5.7	<0.01	0.42	1.26	1.01	0.00	0.26
C-10Q	-	6.1	<0.01	0.46	1.44	1.15	0.00	0.29

*see Table 1
Q = new sample, quartered core

Table 3. General megascopic features of the Waite Amulet core samples

Borehole	Sample Number	Megascopic Features	Special Items	Category
WA-2	-	5 core samples, each 21 cm to 23 cm long		
	C-1	surface sample with scattered vegetation at top, clay-rich for first 5 cm; remainder yellow-orange, ocherous, strongly oxidized and without sulphides		surface sample, strongly oxidized
	C-2	upper quarter stongly oxidized, ocherous, followed by clay-like* second quarter; remainder black, sulphide-bearing	sub-sampled as C-2 top and C-2 bottom (clay-like zone omitted)	contact between leached (sulphide-depleted) and sulphide-rich zones
	C-3	black, sulphide-rich		sulphide zone
	C-4	black, sulphide-rich		sulphide zone
	C-5	black, sulphide-rich		sulphide zone
WA-8	-	10 samples; 16 cm to 18 cm long except for C-5 (13 cm)		
	C-1	surface sample of clay with minor vegetation	carbonate-rich	surface clay
	C-2	surface clay, as above	carbonate-rich	surface clay
	C-3	clay in uppermost third of core, gradational to strongly oxidized, ocherous remainder	clay-rich fraction at top is carbonate-rich and was deleted from chem. sample	clay gradational to strongly oxidized
	C-4	strongly oxidized, ocherous except that last cm is dark grey, sulphide-bearing		strongly oxidized
	C-5 to C-10 incl.	black, sulphide-rich; rind of ocherous material removed from C-5 and C-6		sulphide zone
WA-11	-	15 samples, from 19 cm to 22 cm long		
	C-1	ocherous, strongly oxidized with abundant vegetation at top	sub-sampled as C-1 top and C-1 bottom	strongly oxidized

Table 3. General megascopic features of the Waite Amulet core samples (cont'd.../2)

Borehole	Sample Number	Megascopic Features	Special Items	Category
	C-2	ocherous, strongly oxidized		strongly oxidized
	C-3	upper half oxidized, lower half sulphide-rich; the two are separated by a 1-1.5 cm highly ocherous zone	sub-sampled: top; intermediate strongly ocherous zone; bottom sulphide-rich zone	contact between sulphide-depleted and sulphide-rich zones
	C-4	black, sulphide-rich		sulphide zone
	C-5	black, sulphide-rich, with uppermost quarter very fine-grained	sub-sampled as uppermost quarter, and remainder	sulphide zone
	C-6	grey to black with diffuse, weak oxidation in upper half, gradational downward to strongly oxidized 3-4 cm zone at bottom	sub-sampled as top half, bottom half	local oxidation, paleosurface
	C-7	about 0.5 cm oxidation at top; remainder black, sulphide-rich		mainly sulphide zone
	C-8 to C-15 incl.	black, sulphide-rich		sulphide zone
WA-22	-	sample C-1 15 cm long; all others 17 to 21 cm long		
	C-1	surface sample with abundant vegetation at top; strongly oxidized, but less ocherous than WA-11		strongly oxidized
	C-2	strongly oxidized, better layering than in C-1		strongly oxidized
	C-3	upper half similar to C-2, followed by a 2-3 cm zone of more strongly ocherous material which is gradational downward to black, sulphide-rich material	sub-sampled as top zone, middle ocherous zone, and bottom	transitional from oxidized to sulphide-rich
	C-4	weakly oxidized layers in upper third; remainder black, sulphide-rich		weakly oxidized, mainly sulphide-rich
	C-5 to C-9 incl.	black, sulphide-rich		sulphide zone

Table 3. General megascopic features of the Waite Amulet core samples (cont'd.../3)

Borehole	Sample Number	Megascopic Features	Special Items	Category
WA-17	-	15 samples from 16 cm to 21 cm long		
	C-1	surface sample with 0.5 cm of soil at top and abundant vegetation; remainder strongly oxidized, yellowish brown	0.5 cm soil removed	strongly oxidized
	C-2	strongly oxidized, excellent varve-like layering gradational downward to sandier, thicker layers		strongly oxidized
	C-3	grey to black, sulphide-rich but with local weak oxidation		mainly sulphide-rich
	C-4	black, fine-grained, well-layered		sulphide zone
	C-5	black, well-layered		sulphide zone
	C-6	black, sulphide-rich for 3-3.5 cm, succeeded by a 3-4 cm zone of moderate oxidation along a vegetation-bearing paleosurface, and then 5 cm of black, sulphide-rich; remainder gradational to moderately strongly oxidized, partly ocherous, vegetation-bearing paleosurface		mixed sulphide and oxidized zones at paleosurfaces
	C-7	a 0.5 cm thick, vegetation-bearing, irregular, strongly oxidized yellowish zone near the core top; remainder black, sulphide-rich		mainly sulphide zone
	C-8	black, sulphide-rich; a large vug 2.5 cm long and 5 cm wide is almost the full diameter of the core, but not visibly oxidized		sulphide zone
	C-9	black, sulphide-rich		sulphide zone
	C-10	black, sulphide-rich; a weakly oxidized(?) greenish yellow interior zone		sulphide zone
	C-11 to C-15 incl.	black, layered, normal sulphide-rich		sulphide zone

Table 3. General megascopic features of the Waite Amulet core samples (cont'd.../4)

Bore-hole	Sample Number	Megascopic Features	Special Items	Category
WA-1	-	18 cores, with C-1 to C-9 15 to 18 cm long, and C-10 to C-17 18 cm to 21 long; core C-18 was 26 cm long		
	C-1	surface sample; clay-like with abundant organic material	carbonate-rich	surface clay
	C-2	strongly oxidized, orange-brown ocherous		strongly oxidized
	C-3, C-4	similar to C-2		strongly oxidized
	C-5	less brownish, more yellowish; last 2-3 cm is black		strongly oxidized
	C-6, C-7	black, sulphide-rich, variable from very fine-grained to relatively coarse layers		sulphide zone
	C-8	upper 5-6 cm is strongly oxidized and includes a small amount of organic material; remainder black, friable	sub-sampled into top and bottom zones	oxidized paleo-surface and underlying sulphide zone
	C-9	black, friable upper half similar to that in C-8 but with minor oxidized zone at top; bottom half consists of oxidized interior surrounded by a black shell (proportions of core and shell about 1:1) -- structure suggests that the interior, oxidized material is more representative of the sample site		mixture of oxidized and sulphide-rich zones
	C-10	upper 4 cm strongly oxidized; remainder black, sulphide-rich		mainly sulphide zone
	C-11 to C-18 incl.	black, sulphide-rich		sulphide zone
WA-20	-	upper, strongly oxidized zone progresses downward to unaltered, sulphide-rich zone; see Jambor (1986)		

*Clay-like refers to particle size rather than to composition. Clay-like fractions are composed predominantly of fine-grained tailings silicates.

Table 4. Microscopic characterization of Waite Amulet samples

Drillhole, Sample No.	Relative Grain Size*	Alteration Features	Alteration Intensity
WA-2, C-1	coarse magnetite	strongly oxidized, traces of pyrite (py) and chalcopyrite (cp) are sole sulphides; Fe hydroxide rims numerous	9.5
C-2T*	-	trace sulfides only; Fe hydroxide rims abundant	9.5
C-2B	very fine-grained	mixture of strongly oxidized as above, plus only weakly altered sulphides -- transition zone	1
C-3	very fine-grained	abundant pyrrhotite (po) -pyrite (py); most po intact, but many grains have weakly altered rims	1
C-4	very fine-grained	similar to C-3 but much less altered	0
C-5	coarse with numerous f.g. clumps	negligible alteration of po, but several grains of covellite observed, indicating a probable zone of supergene enrichment	0
WA-8, C-3	coarse	strongly oxidized; trace sulphides (mainly cp); Fe hydroxide rims abundant; traces of covellite	10
C-4	intermediate	texture consists of coarse grains mixed with clumps of very fine-grained material; mainly strongly oxidized as in C-3; some clumps contain py-cp-po, suggesting abrupt contact with unoxidized material	10
C-5	very fine-grained	most po grains fairly fresh, but fine grain size hinders observations; some po grains have thin alteration rims	1-2
C-6	very fine-grained	weak alteration at a few po grain edges	0-0.5
C-7	very fine-grained	similar to C-6	0-0.5
C-8	very fine-grained	similar, but a few grains also show alteration to probable marcasite	0.5
C-9	very fine-grained	scattered coarse grains; only traces of rim alteration	0
C-10	very fine-grained	similar to C-9	0

Table 4. Microscopic characterization of Waite Amulet samples (cont'd.../2)

Drillhole, Sample No.	Relative Grain Size*	Alteration Features	Alteration Intensity
WA-11, C-1T	coarse	low magnetite, trace cp; strongly oxidized	9.5-10
C-1	coarse	similar to C-1T, but Fe hydroxide rims and pseudomorphs more abundant	9.5-10
C-2	coarse	about 1% magnetite, 0.1% cp, both unaltered; strongly oxidized but without Fe hydroxide rims	9
C-3T	coarse	similar to C-2	9
C-3	coarse	less magnetite, but cp still common	9
C-3B	intermediate	scattered coarse grains plus clumps with very fine-grained sulphides; first appearance of py+po with po extensively altered and pseudomorphs common; several grains covellite	6
C-4	intermediate	texture as in C-3B; a few po pseudomorphs but most alteration limited to po rims	4
C-5T	intermediate	upper quarter of core; negligible alteration	0
C-5	coarse	negligible alteration	0
C-6T	intermed.-coarse	mainly coarse grains with numerous clumps containing moderate amounts of very fine-grained sulphides; po variable from fresh to grains with only remnant cores -- suggests a blend of altered and unaltered zones (low alteration rating reflects the higher proportion of fresh grains)	2
C-6B	coarse	predom. strongly oxidized, low sulphide; trace covellite	8
C-7	coarse	negligible alteration	0
C-9	intermediate	negligible alteration	0
C-10	coarse	negligible alteration; scattered strongly altered aggregates, presumably contamination	0

Table 4. Microscopic characterization of Waite Amulet samples (cont'd.../3)

Drillhole, Sample No.	Relative Grain Size*	Alteration Features	Alteration Intensity
C-11	coarse	similar to C-10	0
C-12	intermediate	similar to C-10	0?
C-13	intermediate	similar to C-10; marcasite observed in rare altered grains	0
C-14	intermed.-coarse	similar to C-10	0-0.5
C-15	coarse	altered po rare, mainly to partial rims of marcasite	0-0.5
WA-22, C-1	coarse	well-developed Fe hydroxide rims on silicates and magnetite; several grains cp and a few py, po (a few grains po relatively unaltered-contamination?)	9
C-2	coarse	scattered cp, a few grains py, no po; Fe hydroxide rims less abundant than in C-1	8.5
C-3	coarse	upper part of core; only cp seen	8.5
C-3M	intermediate	mainly fine- to medium-grained clumps with scattered coarse magnetite; py preserved in many of the clumps, Fe hydrox.-jarosite cementation of clumps clearly visible	7
C-3B	coarse	po alteration mainly along parting rather than rims; several grains of covellite observed	3
C-4	coarse	much po weakly to moderately altered; marcasite present	4
C-5	coarse	similar to C-4 but po alteration less intense	3.5
C-6	coarse	po alteration mainly at rims, which include some marcasite	4
C-7	coarse	similar to C-6, including marcasite, but alteration less intense	2.5
C-8	coarse	only scattered grains weakly altered	0-0.5
C-9	coarse	similar to C-8	0-0.5

Table 4. Microscopic characterization of Waite Amulet samples (cont'd.../4)

Drillhole, Sample No.	Relative Grain Size*	Alteration Features	Alteration Intensity
WA-17, C-1	coarse	excellent Fe hydroxide rims on silicates and some magnetite grains; traces of cp, py	9-9.5
C-2	coarse	po present but most grains partly replaced	4
C-3	intermediate	mixed coarse grains with abundant clumps containing fine-grained sulphides; traces of covellite noted in C-2 and C-3; many po grains fresh	2.5
C-4	coarse	similar to C-3 but more po grains altered; traces of covellite present	3
C-5	coarse	similar to C-4	2.5-3
C-6	coarse	similar to C-5	3.5
C-7	coarse	some po grains strongly altered; a few Fe hydroxide rims present on silicates	4
C-8	coarse	numerous clumps with very fine-grained sulphides; alteration mainly at po rims	3.5
C-9	coarse	abundant clumps - texture nearly intermediate; po weakly rim-altered	1
C-10	intermediate	both coarse and fine-grained sulphides abundant; most po fresh, but a few grains moderately altered	0.5
C-11	coarse	clumps with fine- to medium-grained sulphides are abundant; weak rim alteration of some po	0.5
C-12	coarse	C-12 to C-15 inclusive: only traces of alteration, negligible overall	0
C-13	coarse		0
C-14	coarse		0
C-15	coarse		0

Table 4. Microscopic characterization of Waite Amulet samples (cont'd.../5)

Drillhole, Sample No.	Relative Grain Size*	Alteration Features	Alteration Intensity
WA-1, C-2	coarse	oxidized strongly but several grains cp, trace py noted; Fe hydroxide rims abundant, but thin	9.5
C-3	coarse	similar to C-2 but rims more pronounced	10
C-4	coarse	similar to C-3	10
C-5	coarse	similar to C-2	10
C-6	coarse	po abundant, altered variably from pseudomorphs to fresh but majority altered moderately	5
C-7	coarse	po variable from fresh to extensively altered -- high proportion of fresh grains	3.5
C-8T	coarse	po variable from fresh to pseudomorphed	3
C-8B	coarse	alteration variable as in C-8T	2-2.5
C-9	coarse	mixed assemblage, in part strongly oxidized, but many fresh grains	3
C-10	coarse	most po fresh, but Fe hydroxide rims noted on silicates	1
C-11	coarse	negligible alteration	0
C-12	coarse	negligible alteration	0
C-13	coarse	coarse with abundant fine-grained clumps; negligible alteration	0
C-14	coarse	texture as in C-13; negligible alteration	0
C-15	intermed.	negligible alteration	0
C-16	intermed.	fine-grained clumps with numerous dispersed coarse grains as in C-15; alteration negligible	0
C-17	intermed.	similar to C-16	0
C-18	intermed.	similar to C-16	0

*Suffixes: T=top, M=middle,, B=bottom, ox=oxide-rich

Table 5. Chemical analyses and calculated SO_4 distributions in Waite Amulet tailings

Drillhole, Sample No.	pH	Chem. Anal., Water-Soluble Fraction (wt.%)			Calculated Distributions (wt.%)			Chem. Anal., Whole Sample		Total SO_4 Minus Water-Solub SO_4
		Fe	Ca	SO_4	SO_4 as $CaSO_4$	SO_4 as $FeSO_4$	Remnant SO_4	elemental S(wt%)	Total SO_4 (wt%)	
WA-2, C-1	4.2	<0.01	1.00	2.49	2.40	0.00	0.09	<0.01	4.67	2.18
C-2T*	3.8	0.01	0.90	2.46	2.16	0.02	0.30	0.06	4.22	1.76
C-3	4.0	0.15	0.84	3.00	2.01	0.26	0.99	0.12	3.15	0.15
C-4	4.1	0.15	0.71	2.58	1.70	0.26	0.88	0.01	3.09	0.51
C-5	4.2	0.02	0.69	1.92	1.66	0.03	0.26	0.08	2.13	0.21
WA-8, C-2	8.0	0.01	0.16	0.09	0.38	0.02	-	0.06	0.12	0.03
C-3	6.3	<0.01	1.40	3.42	3.36	0.00	0.06	0.19	5.48	2.06
C-4	4.1	<0.01	0.68	1.89	1.63	0.00	0.26	0.05	4.13	2.24
C-5	4.5	0.07	0.44	1.86	1.05	0.12	0.69	0.23	2.28	0.42
C-6	4.8	0.13	0.33	1.68	0.79	0.22	0.67	0.26	2.37	0.69
C-8	4.8	0.13	0.46	1.98	1.10	0.22	0.66	0.42	2.67	0.69
C-9	4.3	0.07	0.39	2.07	0.94	0.12	1.01			
C-10	5.7	<0.01	0.42	1.65	1.01	0.00	0.64			
WA-11, C-1T	3.8	<0.01	0.08	0.06	0.19	0.00	-	0.03	2.40	2.34
C-1	4.2	<0.01	0.22	0.54	0.53	0.00	0.01	0.01	3.33	2.79
C-2	3.8	<0.01	0.72	1.77	1.73	0.00	0.04	0.04	4.74	2.97
C-3T	3.6	<0.01	0.46	1.23	1.10	0.00	0.13	0.07	3.81	2.58
C-3ox	3.4	0.07	0.72	2.52	1.73	0.12	0.67	0.30	6.26	3.74
C-3	4.3	0.23	0.52	1.92	1.25	0.40	0.27	0.88	2.64	0.72
C-4	4.6	0.20	0.33	1.50	0.79	0.34	0.37	0.16	2.61	1.11
C-5	4.7	0.09	0.12	0.69	0.29	0.15	0.25	0.12	1.05	0.36
C-6T	4.5	0.14	0.38	1.44	0.91	0.24	0.29	0.16	2.79	1.35
C-6B	4.3	0.02	0.42	1.14	1.01	0.03	0.10	0.04	3.63	2.49
C-7	5.8	<0.01	0.19	0.60	0.46	0.00	0.14	0.13	0.72	0.12
C-11	5.1	0.01	0.71	1.98	1.70	0.02	0.26	0.05	1.98	0.00
C-15	4.8	<0.01	0.27	0.81	0.65	0.00	0.16	0.08	0.84	0.03
WA-22, C-1	3.8	<0.01	0.05	0.23	0.12	0.00	0.11	0.40	1.26	1.03
C-2	3.7	<0.01	0.32	0.87	0.77	0.00	0.10	0.33	2.13	1.26
C-3	3.5	0.01	0.52	1.35	1.25	0.02	0.08	0.61	3.06	1.71
C-3M	3.3	0.03	1.09	3.06	2.61	0.05	0.40	0.29	5.90	2.40
C-4	4.2	0.03	0.29	0.87	0.70	0.05	0.12	0.25	1.14	0.27
C-6	4.4	0.05	0.41	1.20	0.98	0.09	0.13	0.04	2.01	0.81
C-9	5.0	<0.01	0.33	0.93	0.79	0.00	0.14	0.14	0.99	0.06
WA-17, C-1	4.5	<0.01	0.74	1.77	1.77	0.00	0.00	0.09	4.10	2.33
C-2	4.1	0.01	0.85	2.16	2.04	0.02	0.10	0.25	3.63	1.47
C-3	4.5	0.03	0.38	1.20	0.91	0.05	0.24	0.19	1.74	0.54
C-4	4.2	0.02	0.28	0.99	0.67	0.03	0.29	0.15	1.95	0.96
C-6	4.3	0.01	0.44	1.26	1.05	0.02	0.19	0.19	2.07	0.81
C-9	4.5	0.03	0.55	1.53	1.32	0.05	0.16	0.17	1.65	0.12
C-14	5.0	<0.01	0.07	0.21	0.17	0.00	0.04	0.25	0.24	0.03

Table 5. Chemical analyses and calculated SO_4 distributions in Waite Amulet tailings (cont'd/2

Drillhole, Sample No.	pH	Chem. Anal., Water-Soluble Fraction (wt.%)			Calculated Distributions (wt.%)			Chem. Anal., Whole Sample		Total SO_4 Minus Water-Solubl SO_4
		Fe	Ca	SO_4	SO_4 as $CaSO_4$	SO_4 as $FeSO_4$	Rem-nant SO_4	ele-mental S(wt%)	Total SO_4 (wt%)	
WA-1, C-2	4.5	<0.01	0.73	1.68	1.75	0.00	0.00	0.16	3.72	2.04
C-3	3.9	<0.01	0.67	1.62	1.60	0.00	0.01	0.26	3.92	2.30
C-4	3.4	<0.01	0.57	1.50	1.37	0.00	0.13	1.47	4.46	2.96
C-5	3.7	0.01	0.43	1.14	1.03	0.02	0.09	0.18	3.75	2.61
C-6	4.3	0.04	0.35	1.08	0.84	0.07	0.17	0.20	1.31	0.33
C-7	4.4	0.10	0.14	0.66	0.34	-	-	0.32	1.59	0.93
C-8T*	4.6	<0.01	0.60	1.44	1.44	0.00	0.00	0.28	3.06	1.62
C-8B*	4.3	0.11	0.13	0.66	0.31	0.19	0.16	0.33	1.86	1.20
C-9	4.2	0.04	0.39	1.20	0.93	0.07	0.20	0.32	2.70	1.50
C-10	4.6	0.02	0.31	1.02	0.74	0.03	0.25	0.09	1.89	0.87
C-11	5.3	<0.01	0.12	0.36	0.29	0.00	0.07	<0.01	0.45	0.09
C-16	4.4	0.03	0.52	1.53	1.25	0.05	0.23	<0.01	1.71	0.18

*Suffixes: T=top, M=middle, B=bottom, ox=oxide-rich

Table 6. Electron microprobe analyses of ferrihydrite in Waite Amulet tailings

		1	2
wt. %	Fe_2O_3	62.1	68.9
	Al_2O_3	0.9	0.4
	SiO_2	0.6	0.6
	SO_3	14.2	13.8
	Total	77.8	83.7
	(H_2O)	22.2	16.3

Sample WA-2, C-2T; grain mount

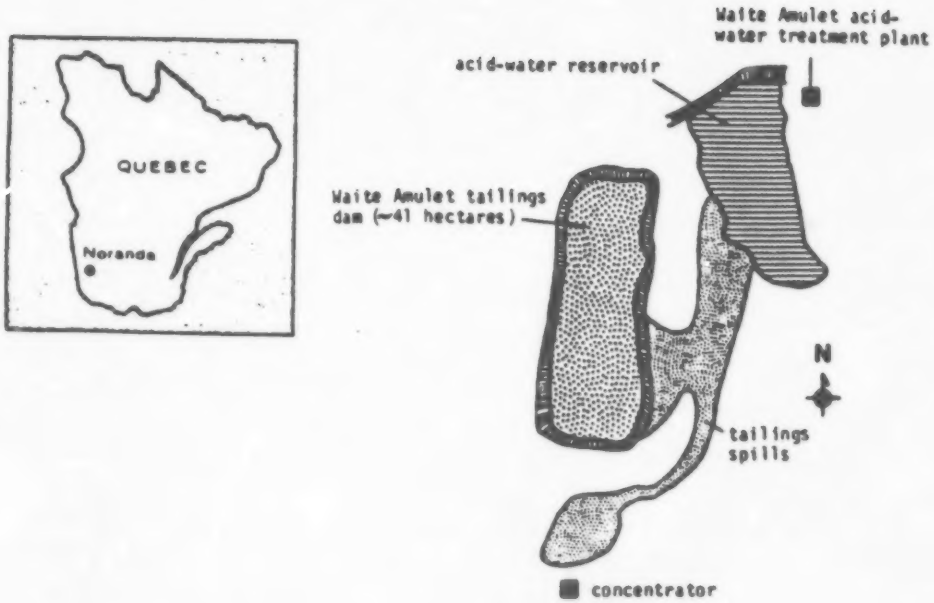


Fig. 1. General configuration of the Waite Amulet tailings dam and minesite.

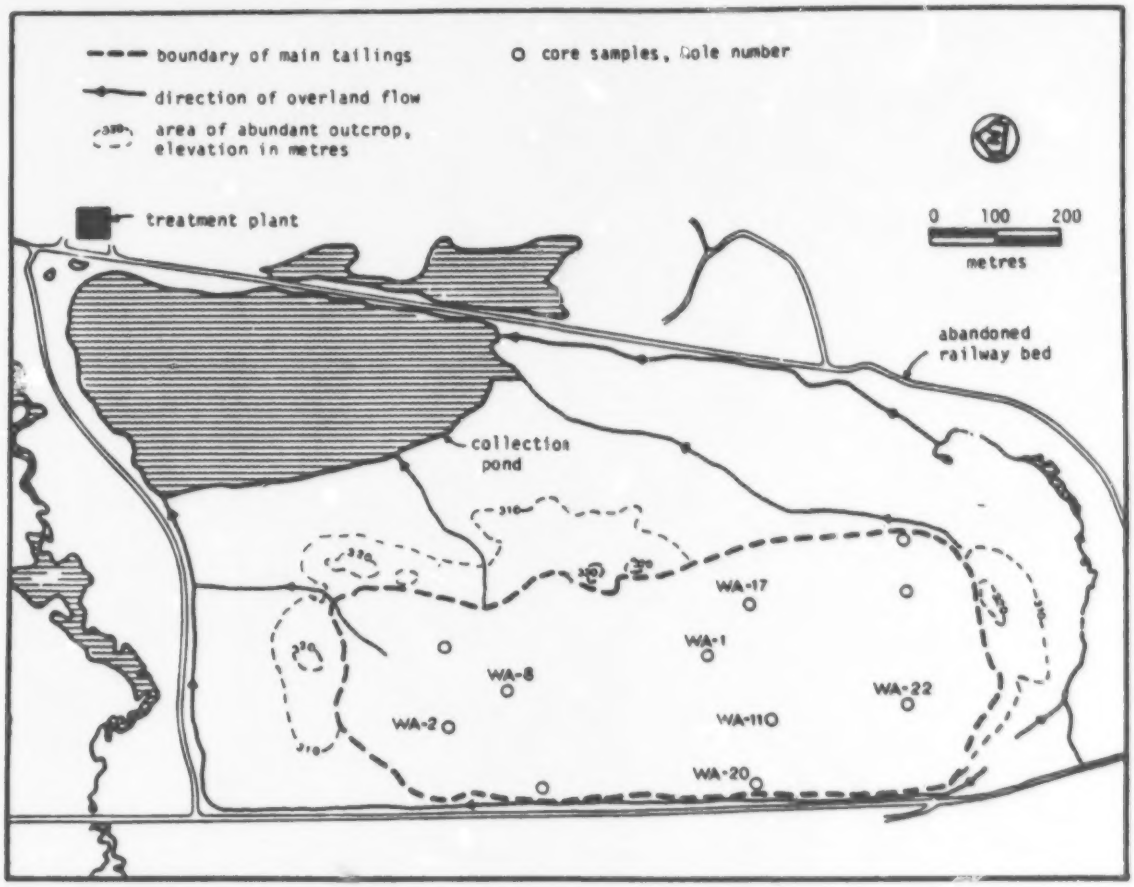


Fig. 2. Waite Amulet tailings pile and drainage pattern. Cored boreholes are shown by open circles; those with numbers were investigated in this study (except WA-20, which was described by Jambor 1986).

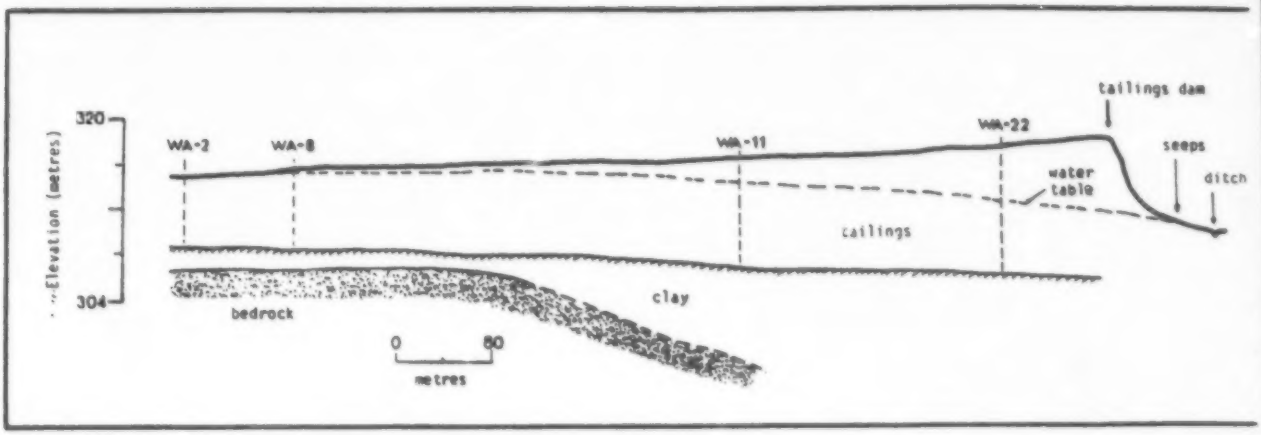


Fig. 3. Longitudinal section of the Waite Amulet tailings, showing the boreholes from which cores have been studied mineralogically. Borehole locations are shown in Figure 2.

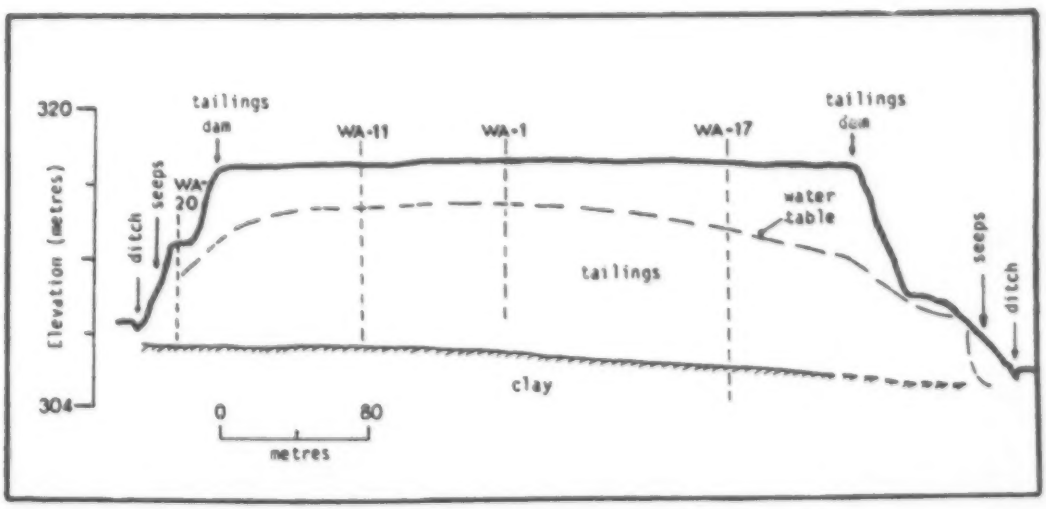


Fig. 4. Cross-section of the Waite Amulet tailings; section is approximately normal to the longitudinal section of Figure 3. Borehole locations are shown in Figure 2.

Fig. 5. Photographs of cores of Waite Amulet tailings. Tops face upward and bar scale at bottom right represents approximately 20 mm.

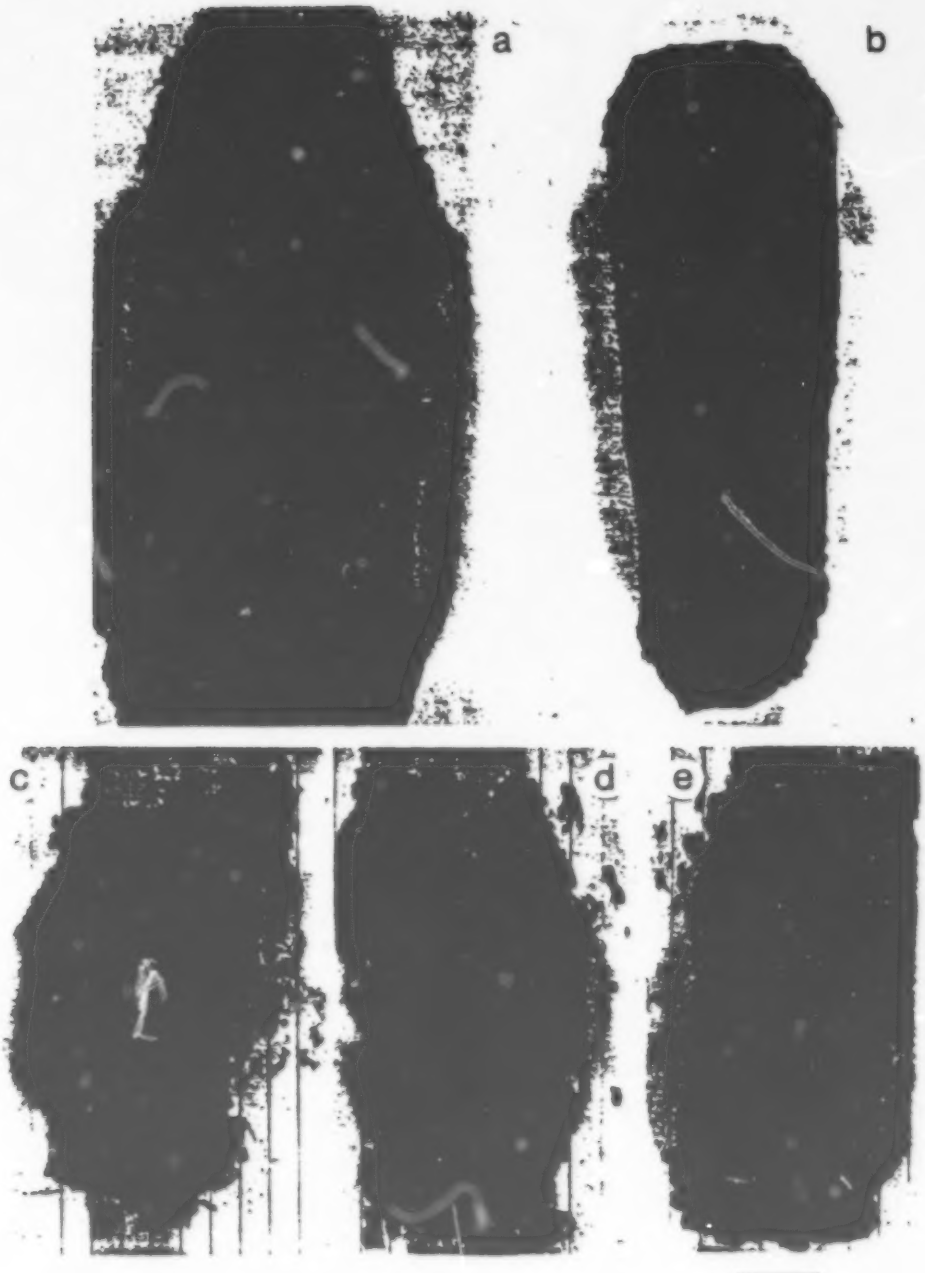
(a) WA-1, C-1, showing dark, vegetation-rich top underlain by lighter, massive clay-like fraction containing abundant calcite.

(b) WA-1, C-3, showing sand-sized tailings with bedding evident from darker, iron-stained layers.

(c) WA-17, C-1T, showing regolith-like top of tailings; vegetation-rich uppermost part was removed, but spicule-like remnants can be seen at right.

(d) WA-17, C-1B, which underlies (c) and is part of the same core, showing relatively thick oxide-rich (dark) and oxide-poor (light) layers.

(e) WA-17, C-2, showing bedded tailings similar to (d), but gradational to coarser, cross-bedded fraction at bottom.


a
b
c
d
e

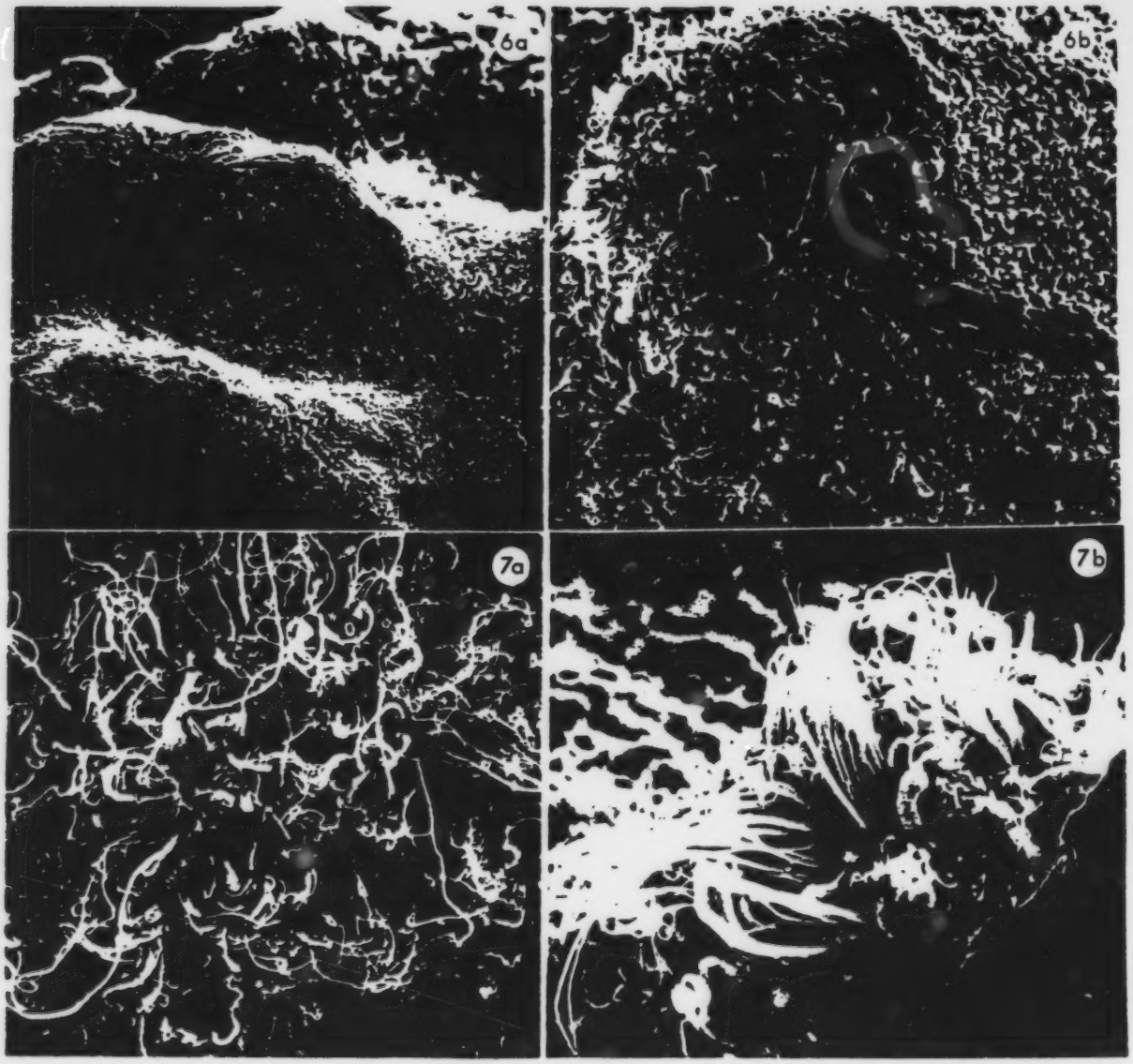


Fig. 6. SEM photographs of (a) radial array of gypsum which crystallized during drying of the core and precipitated on the broken core surface; (b) gypsum rosette from the same sample (WA-8, C-6).

Fig. 7. SEM photographs of filiform magnesian ferrohexahydrite, $(Fe,Mg)SO_4.6H_2O$, formed during drying of core WA-8, C-6. (a) Tangled hair-like mass on core surface; (b) side view showing upright growth from core surface.

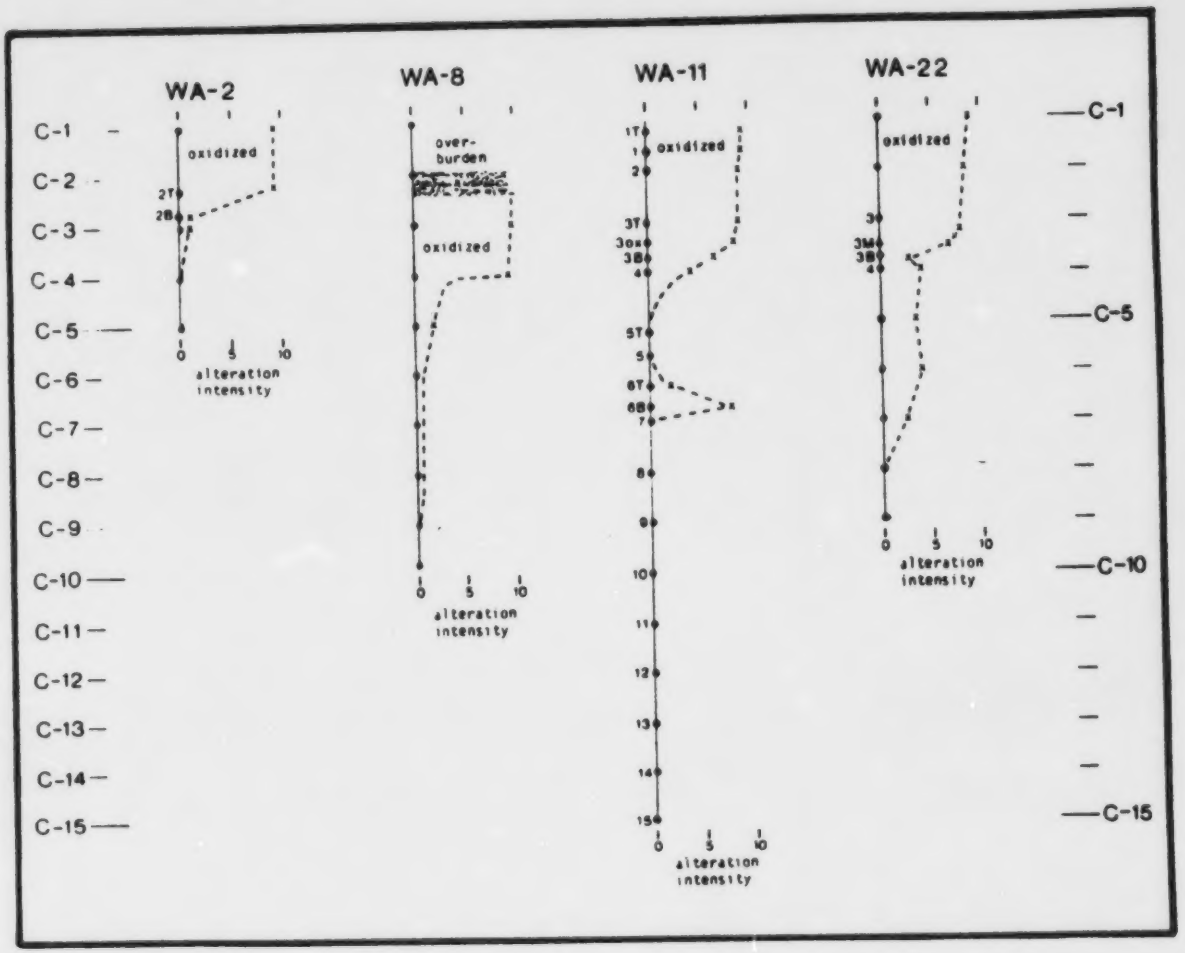


Fig. 8. Alteration intensity of cores from the longitudinal section of the tailings pile (Fig. 2). For Figures 8 to 19, inclusive, the vertical scale is based on sample numbers (C-1 to C-15) because exact sample depths were not provided; dots along borehole length represent relative positions of core samples, and x's indicate intensity of alteration as determined microscopically.

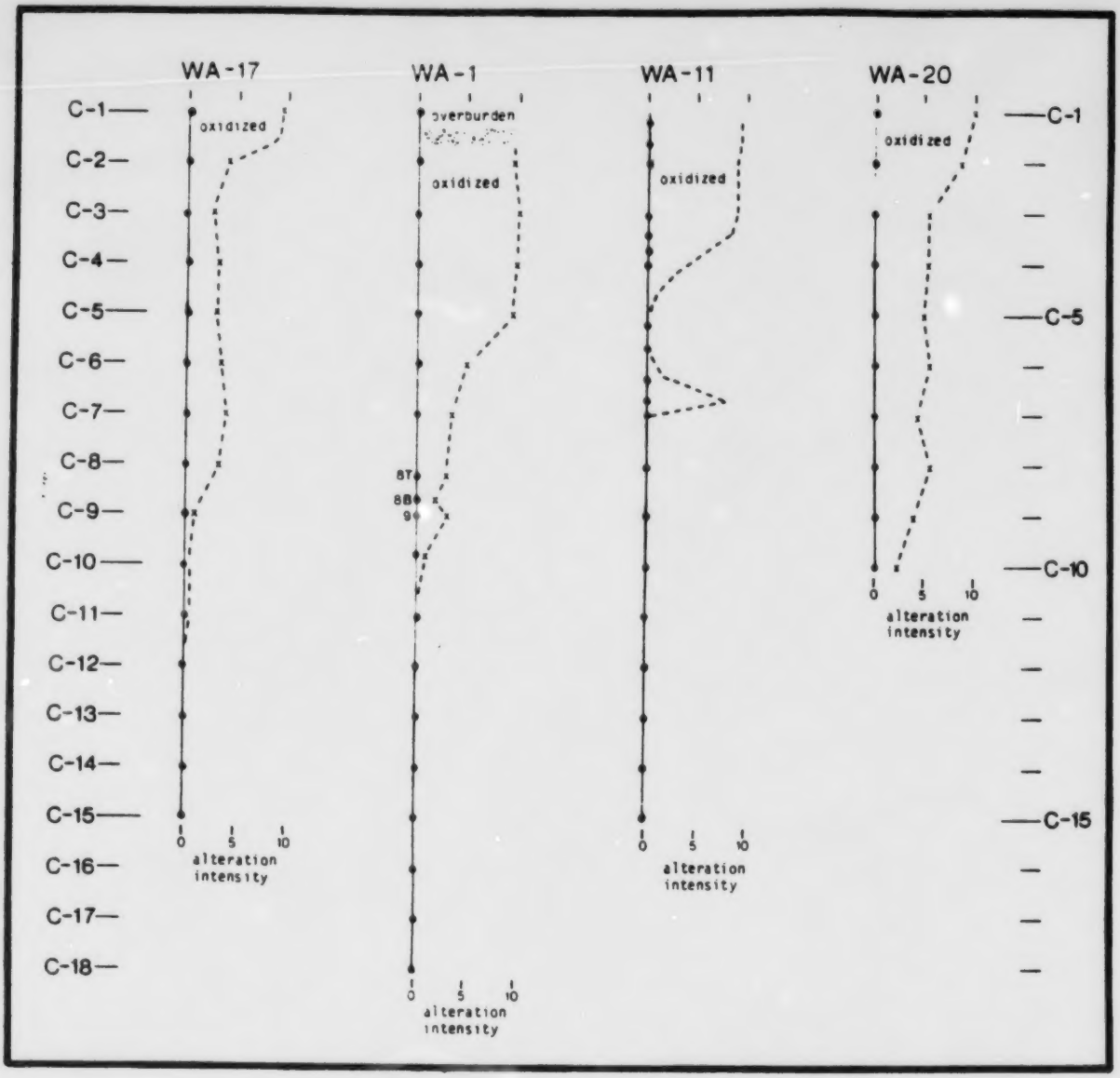


Fig. 9. Microscopically determined alteration intensity in the cross-section of the tailings pile (Fig. 2). Details are explained in the caption for Fig. 8.

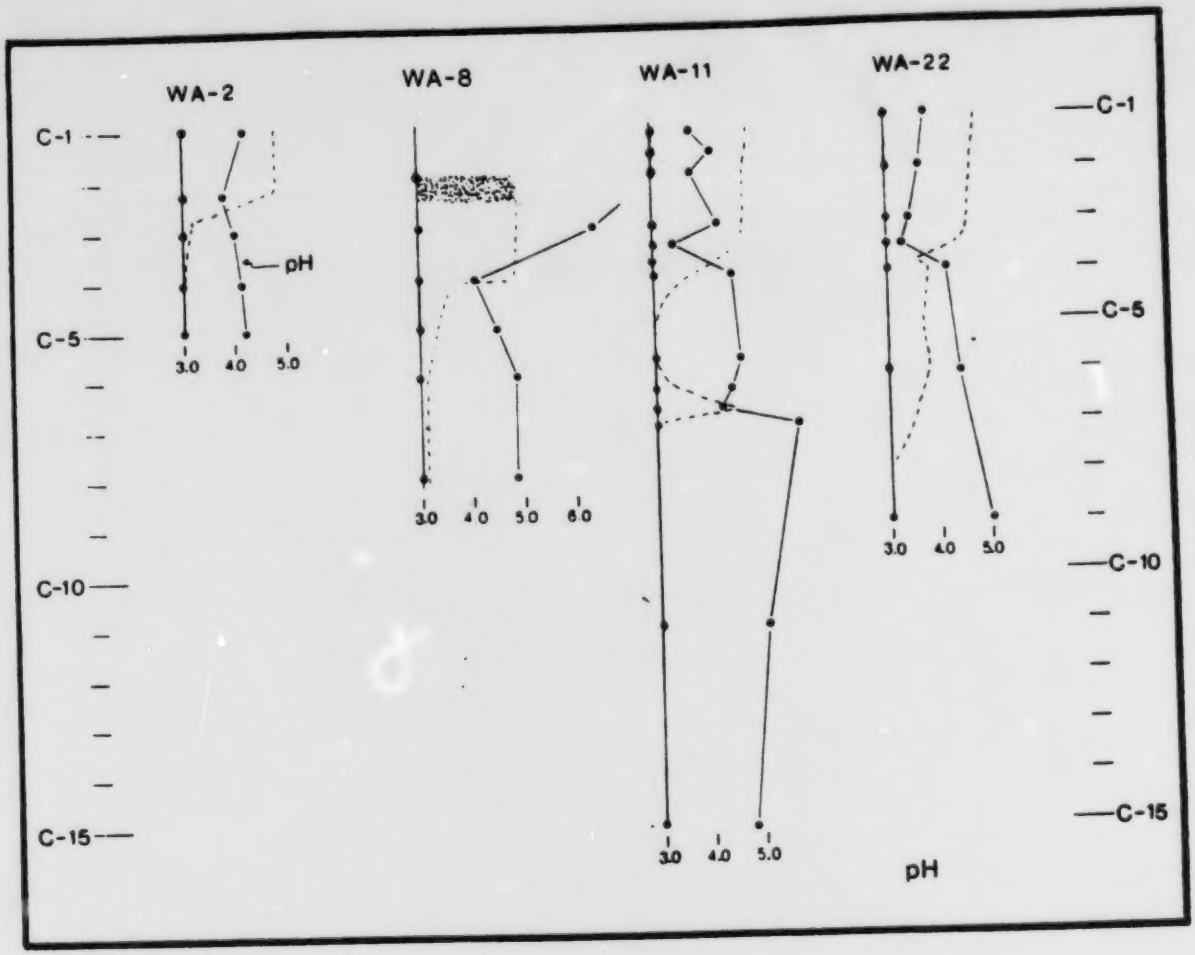


Fig. 10. Variations in pH for the water-soluble fraction in samples from the Waite Amulet longitudinal section. Finely dashed line represents alteration intensity as shown in Figure 8.

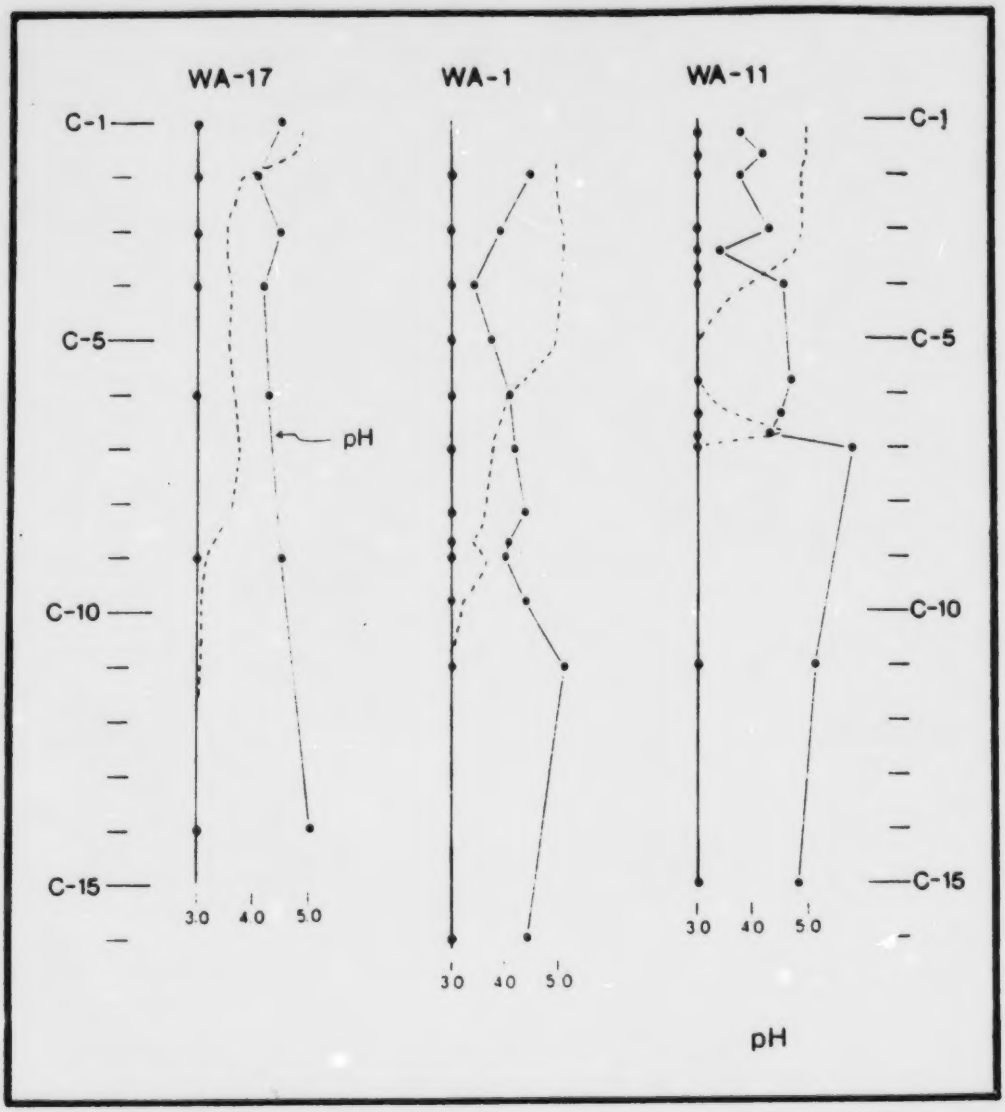


Fig. 11. Variations in pH for the water-soluble fraction in samples from the Waite Amulet cross-section. Finely dashed line represents alteration intensity as shown in Figure 9.

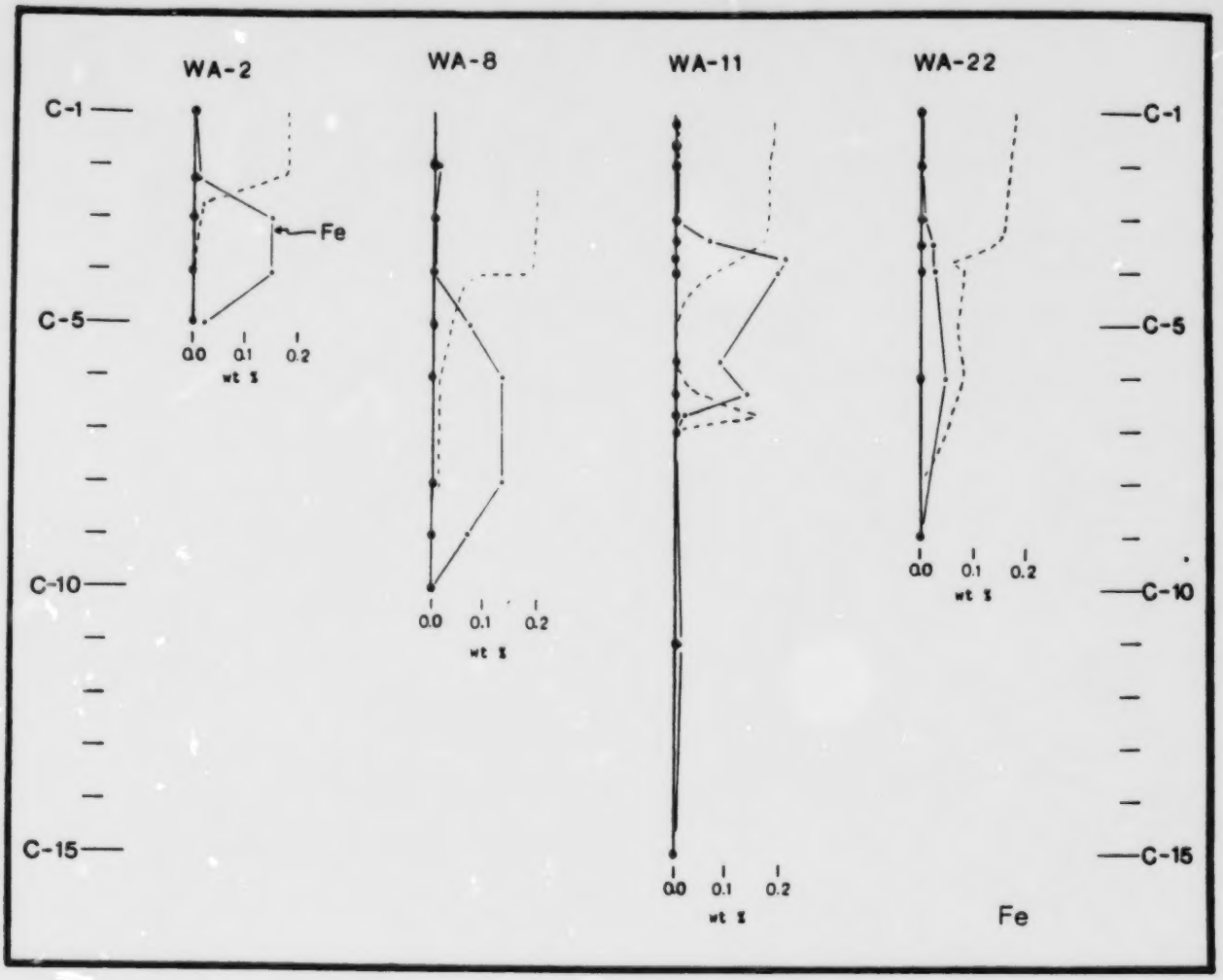


Fig. 12. Variations in wt. % Fe in the water-soluble fraction of samples from the Waite Amulet longitudinal section.

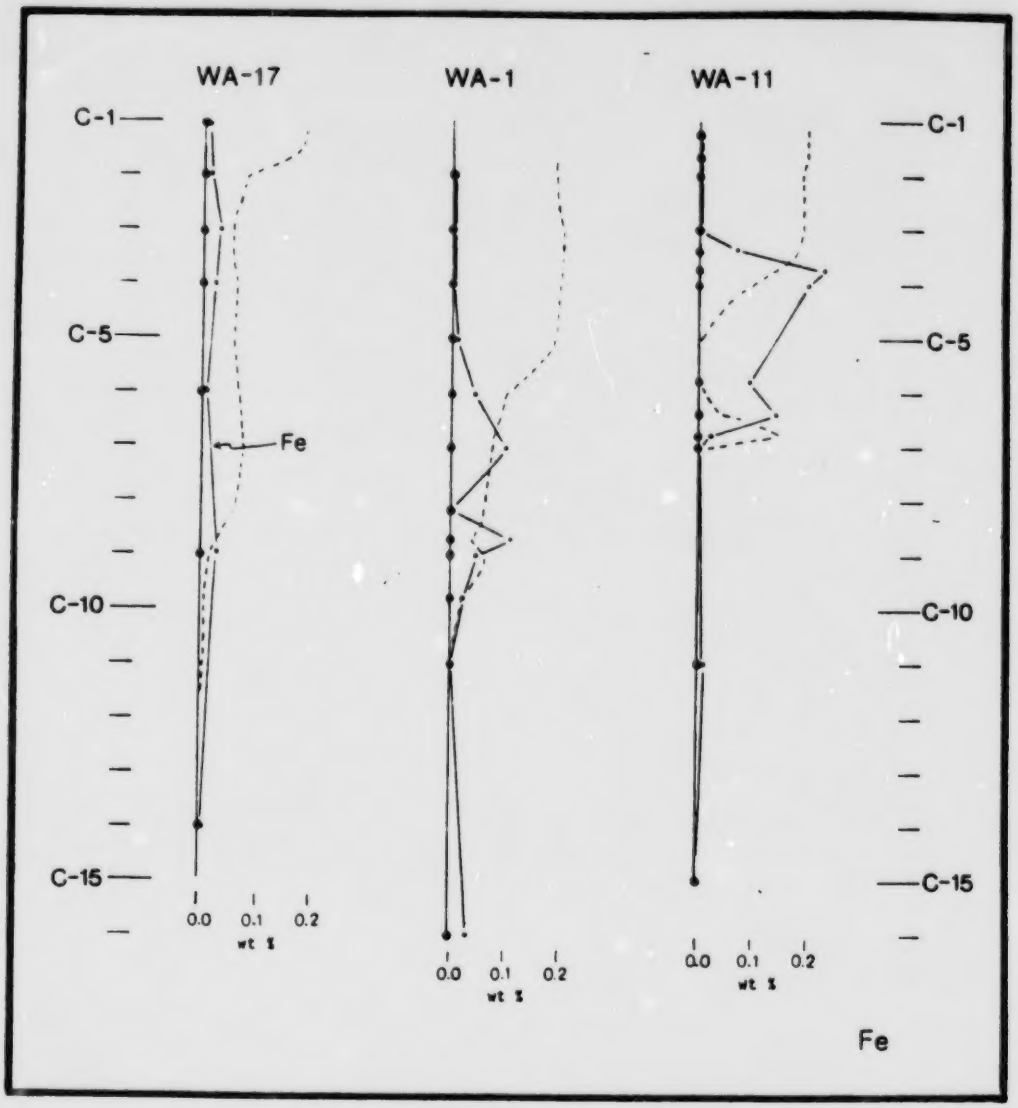


Fig. 13. Variations in wt. % Fe in the water-soluble fraction of samples from the Waite Amulet cross-section.

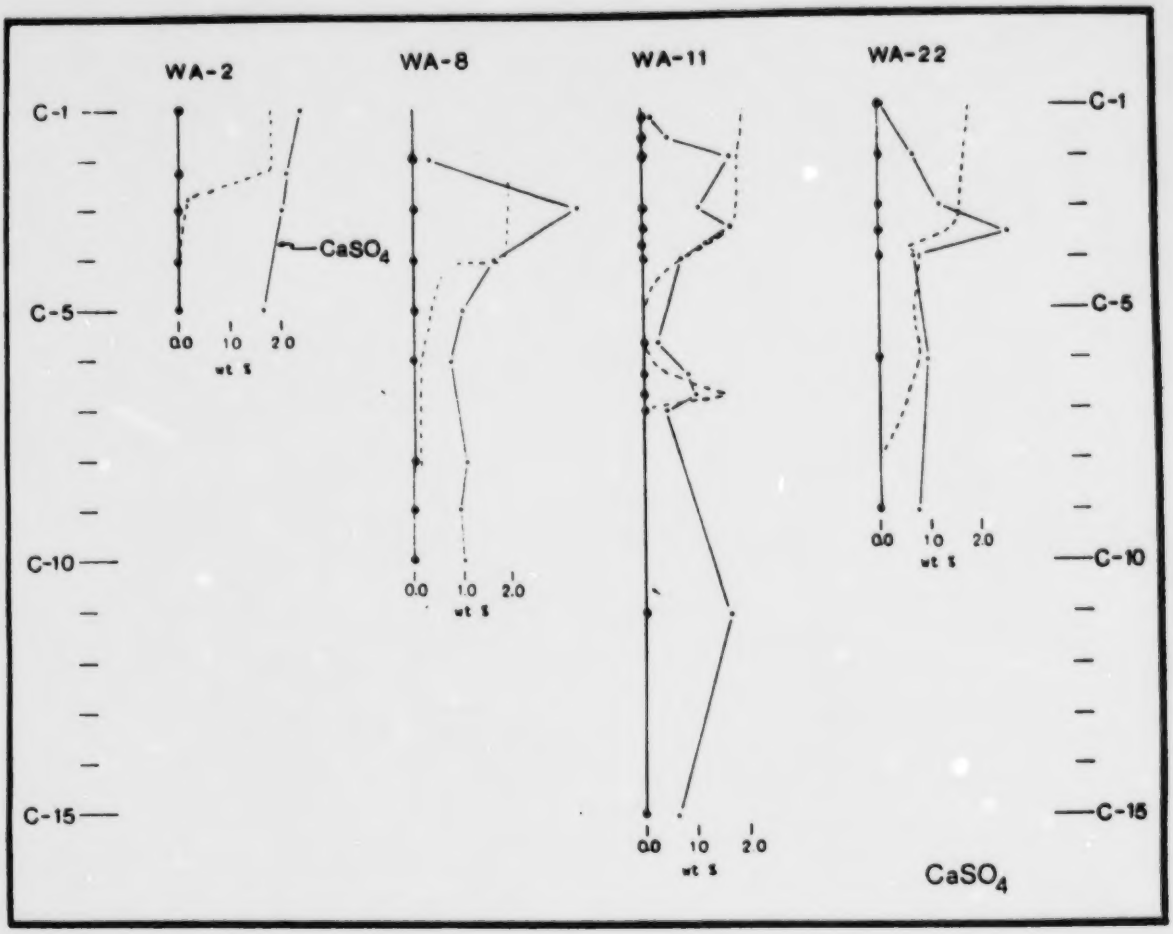


Fig. 14. Variations in wt. % $CaSO_4$ as calculated from Ca contents of the water-soluble fraction in samples from the Waite Amulet longitudinal section.

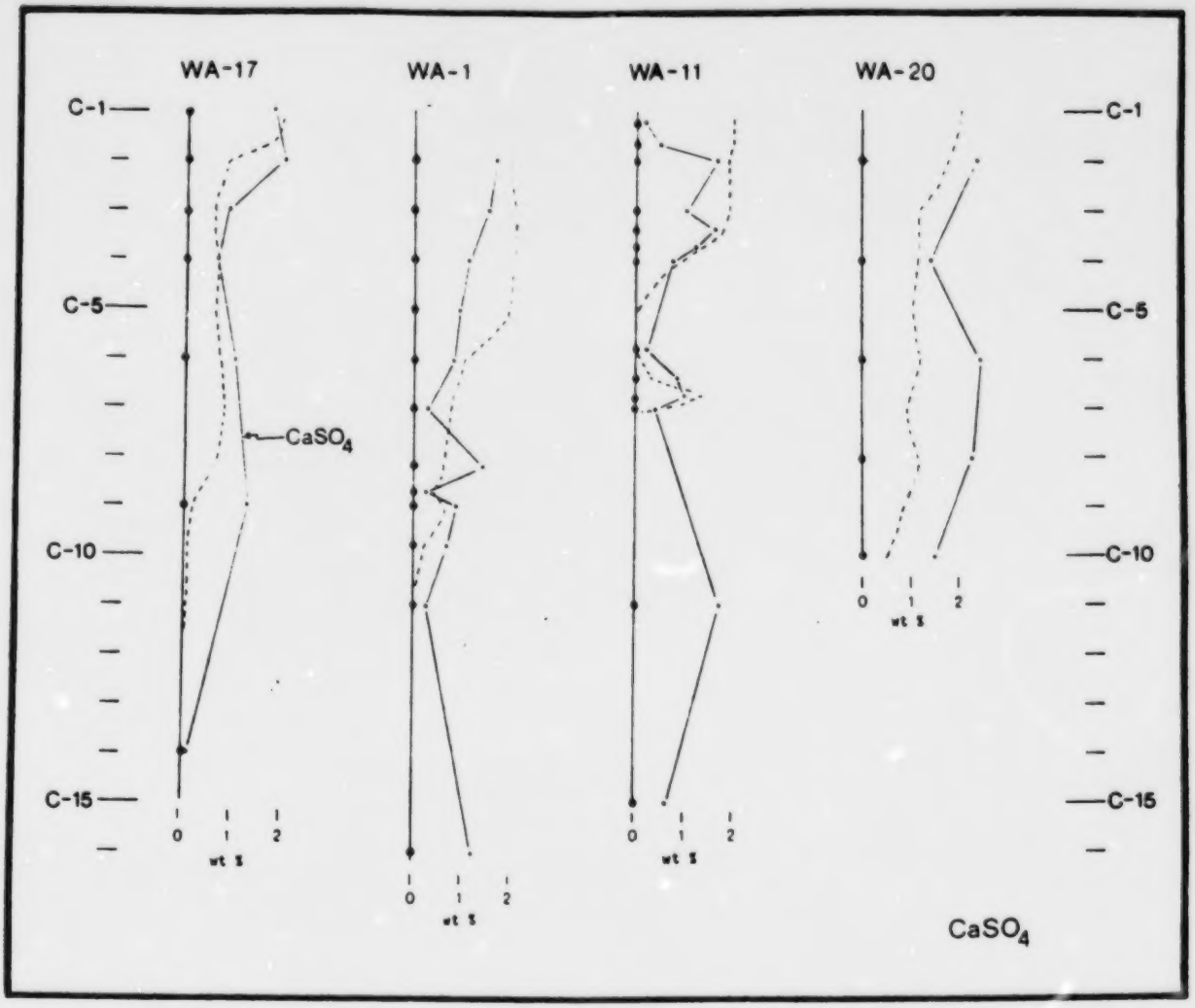


Fig. 15. Variations in wt. % $CaSO_4$ as calculated from Ca contents of the water-soluble fraction in samples from the Waite Amulet cross-section.

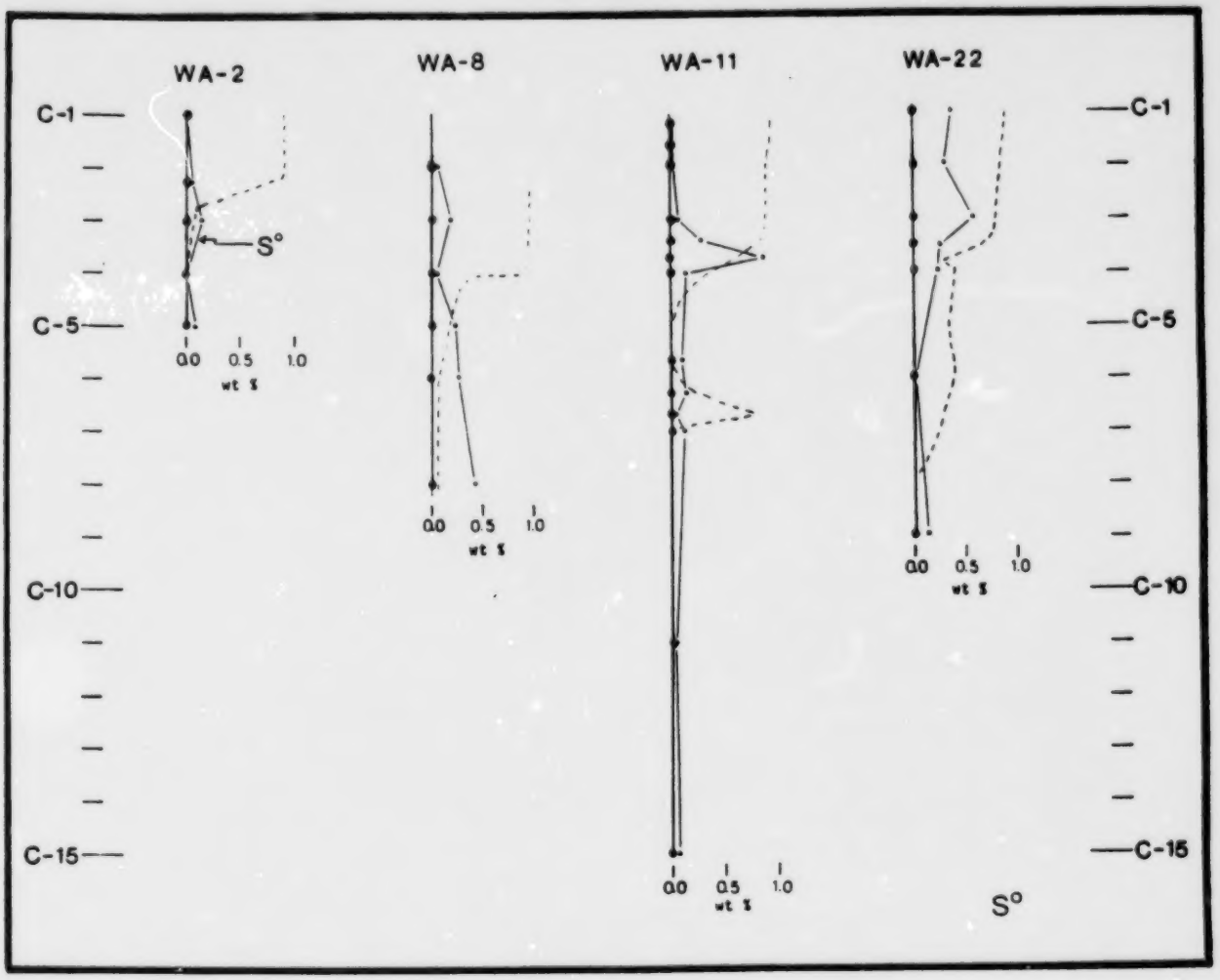


Fig. 16. Variations in wt. % elemental sulphur in samples from the Waite Amulet longitudinal section.

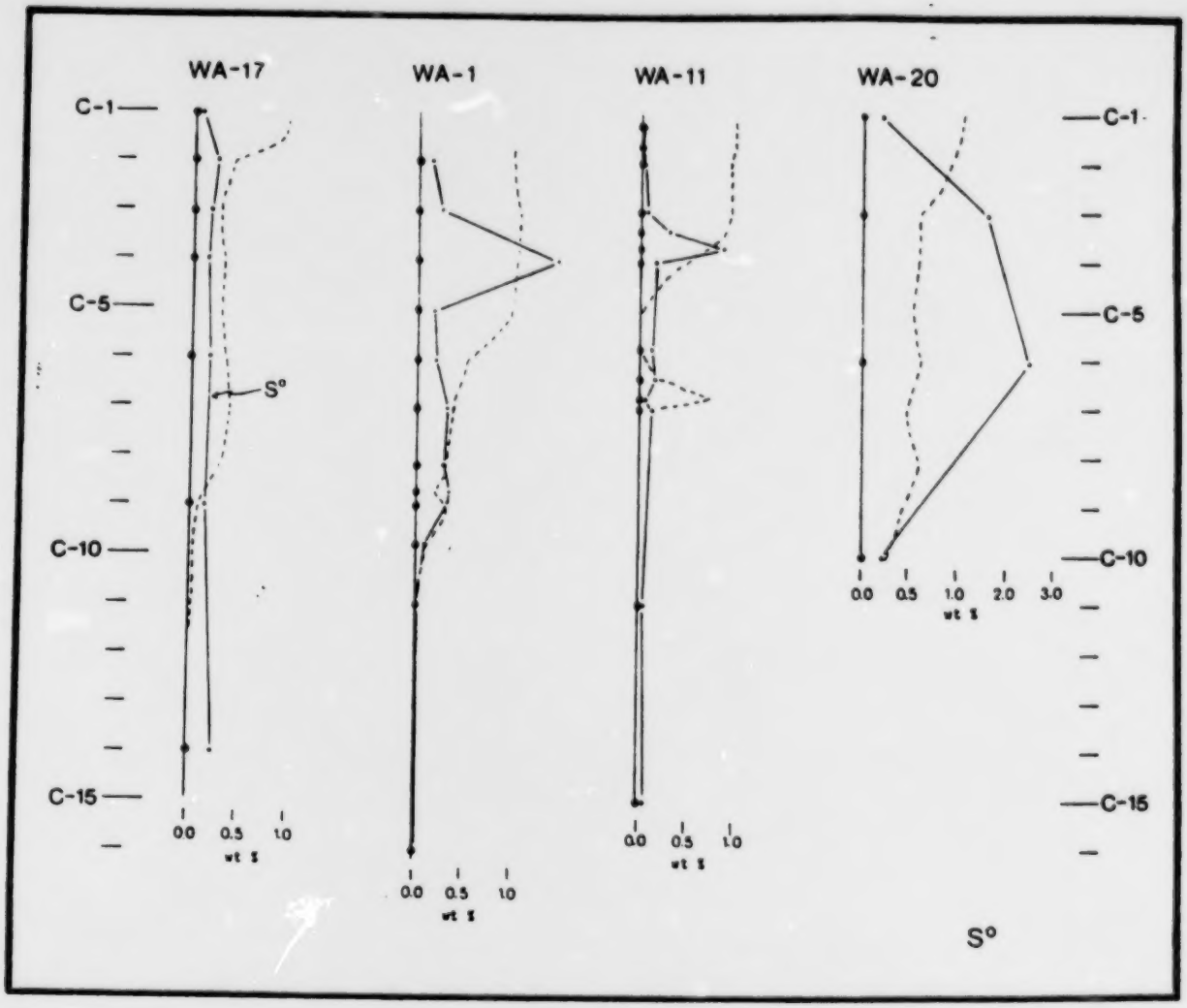


Fig. 17. Variations in wt.% elemental sulphur in samples from the Waite Amulet cross-section.

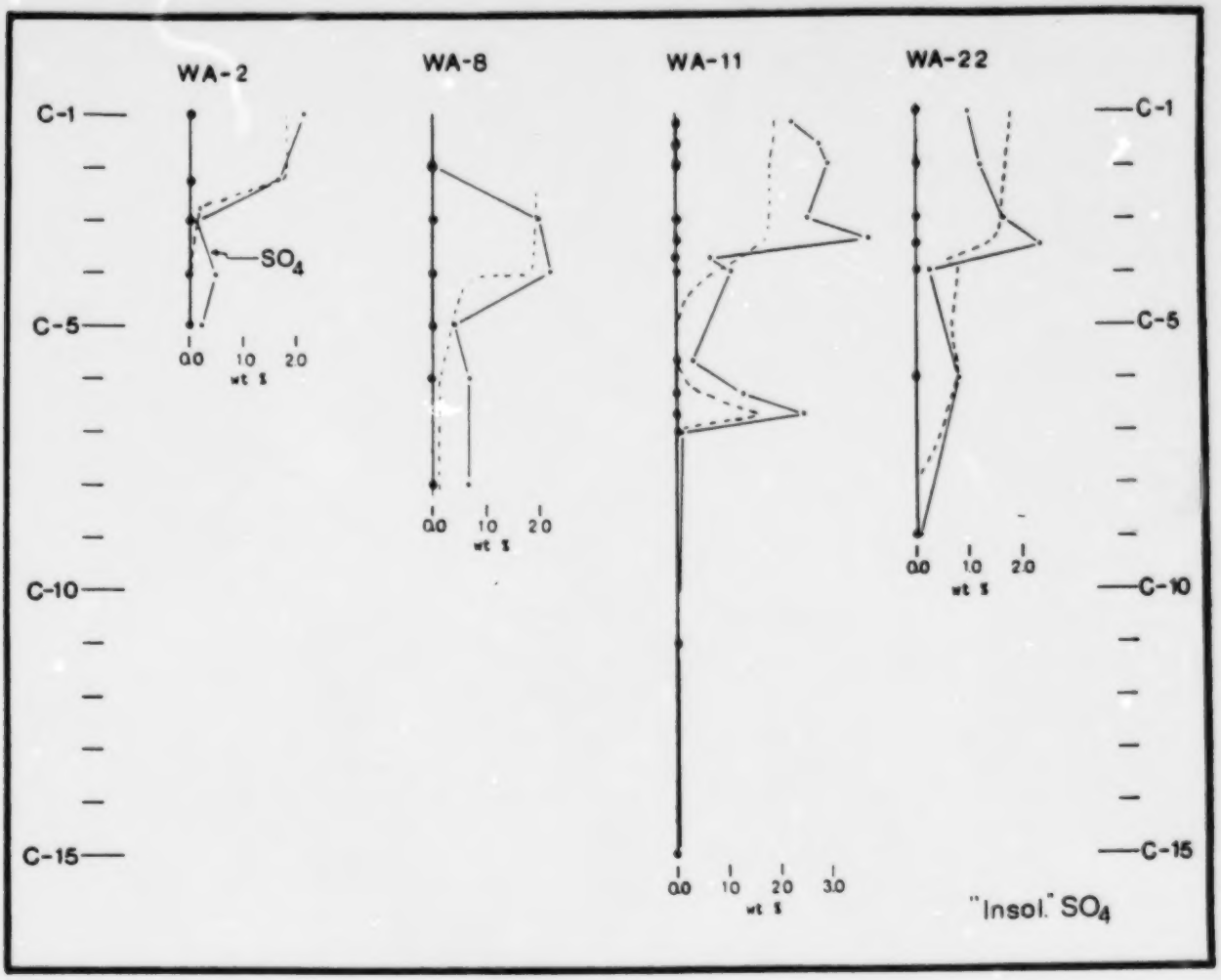


Fig. 18. Variations in SO_4, excluding the water-soluble fraction, in the Waite Amulet longitudinal section. The values basically represent the sulphate that has been precipitated as jarosite.

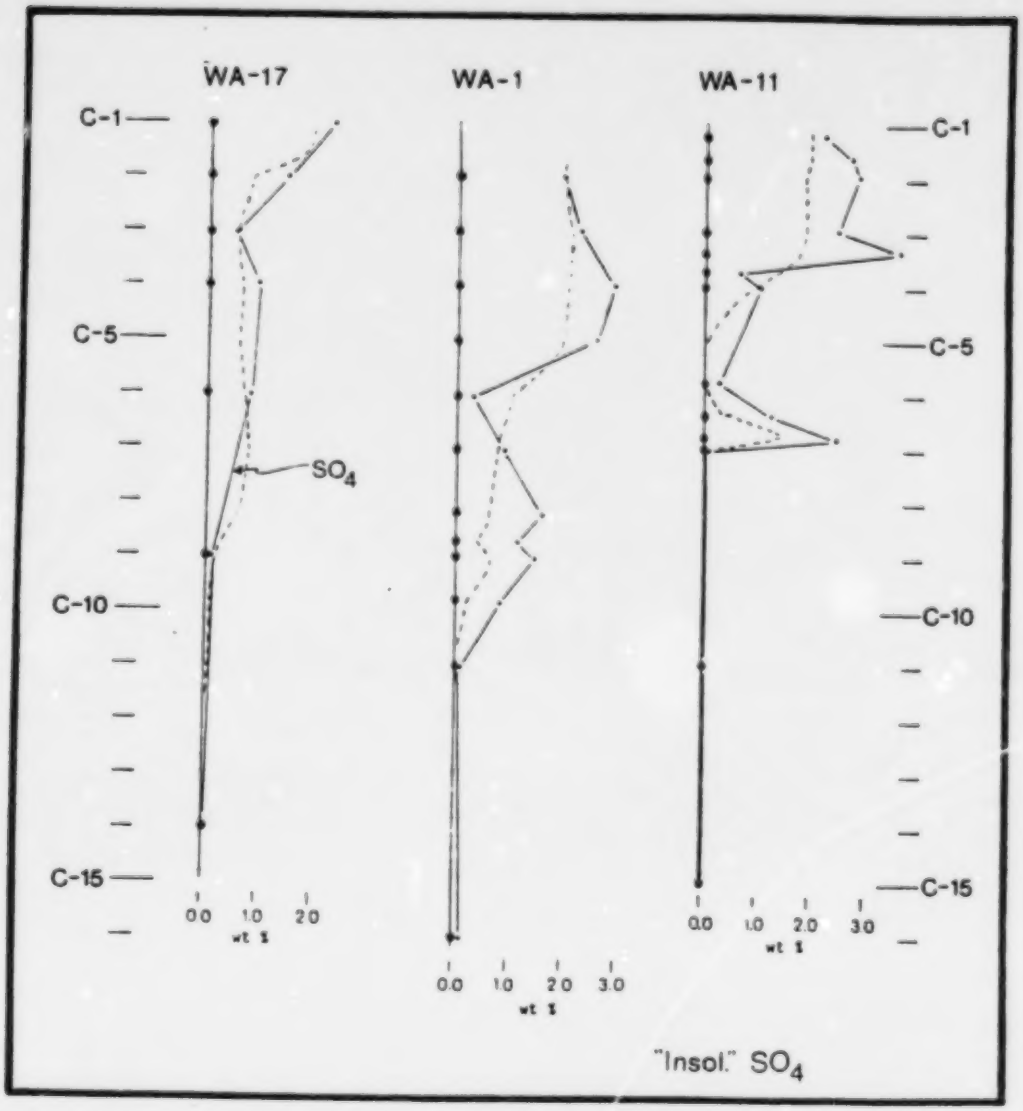


Fig. 19. Variations in SO_4, excluding the water-soluble fraction, in the Waite Amulet cross-section. The values basically represent the sulphate that has been precipitated as jarosite (Fig. 20).

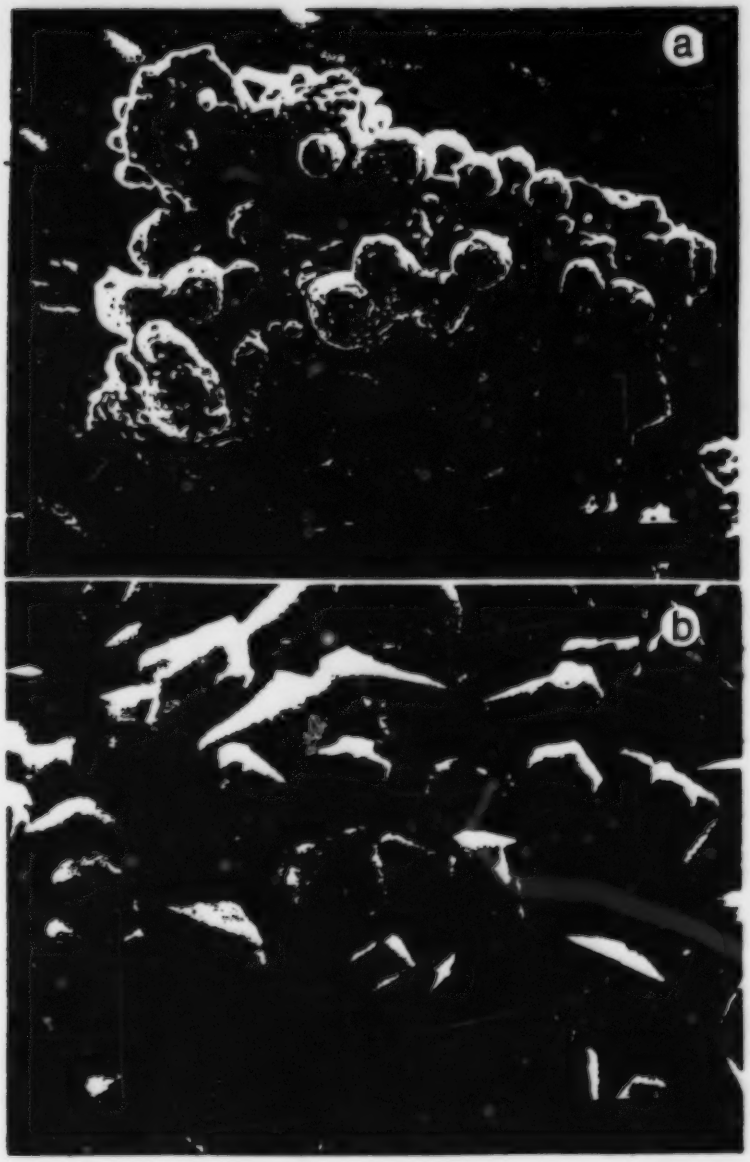


Fig. 20. (a) SEM photograph showing jarosite spheres consisting of fine-grained crystal aggregates; jarosite also occurs in the matrix, cementing the tailings particles. (b) Higher magnification, showing well-formed crystals on the same sample, WA-1, C-4.

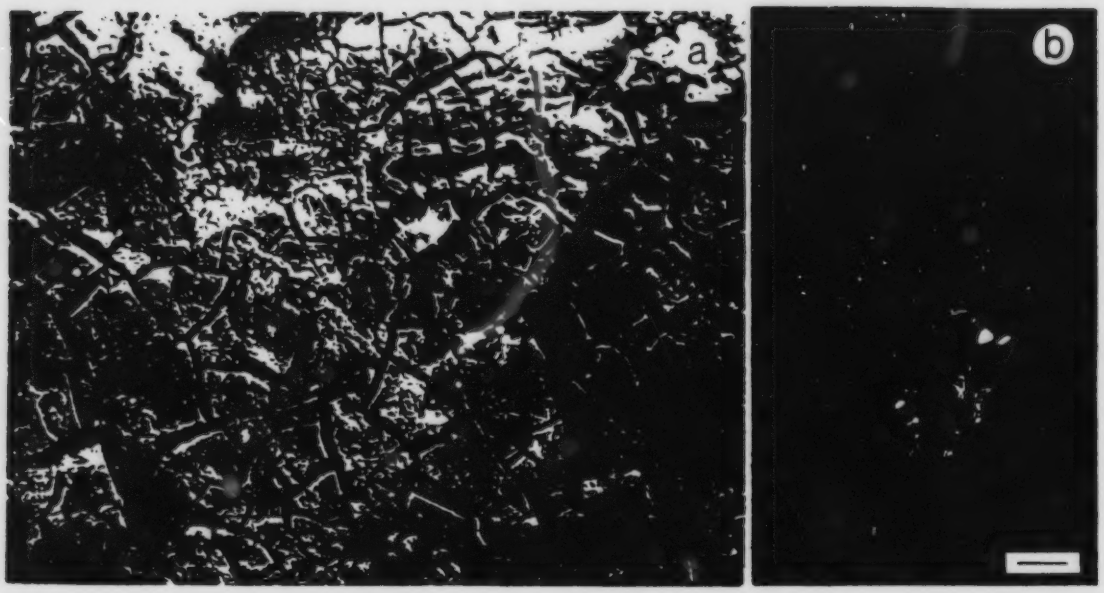


Fig. 21. (a) SEM photograph of ferrihydrite showing "mud-crack" texture characteristic of dehydration. (b) Ferrihydrite capping on a tailings clump; polished section, reflected light; bar scale represents 0.05 mm. Both photos are of sample WA-3, C-2T.

Fig. 22. SEM photograph of euhedral, elongate crystals of unidentified Ca-Fe sulphate mineral associated with anhedral gypsum in sample WA-11, C-3.

APPENDIX C

PROFILES OF PURE GAS OXYGEN CONCENTRATION

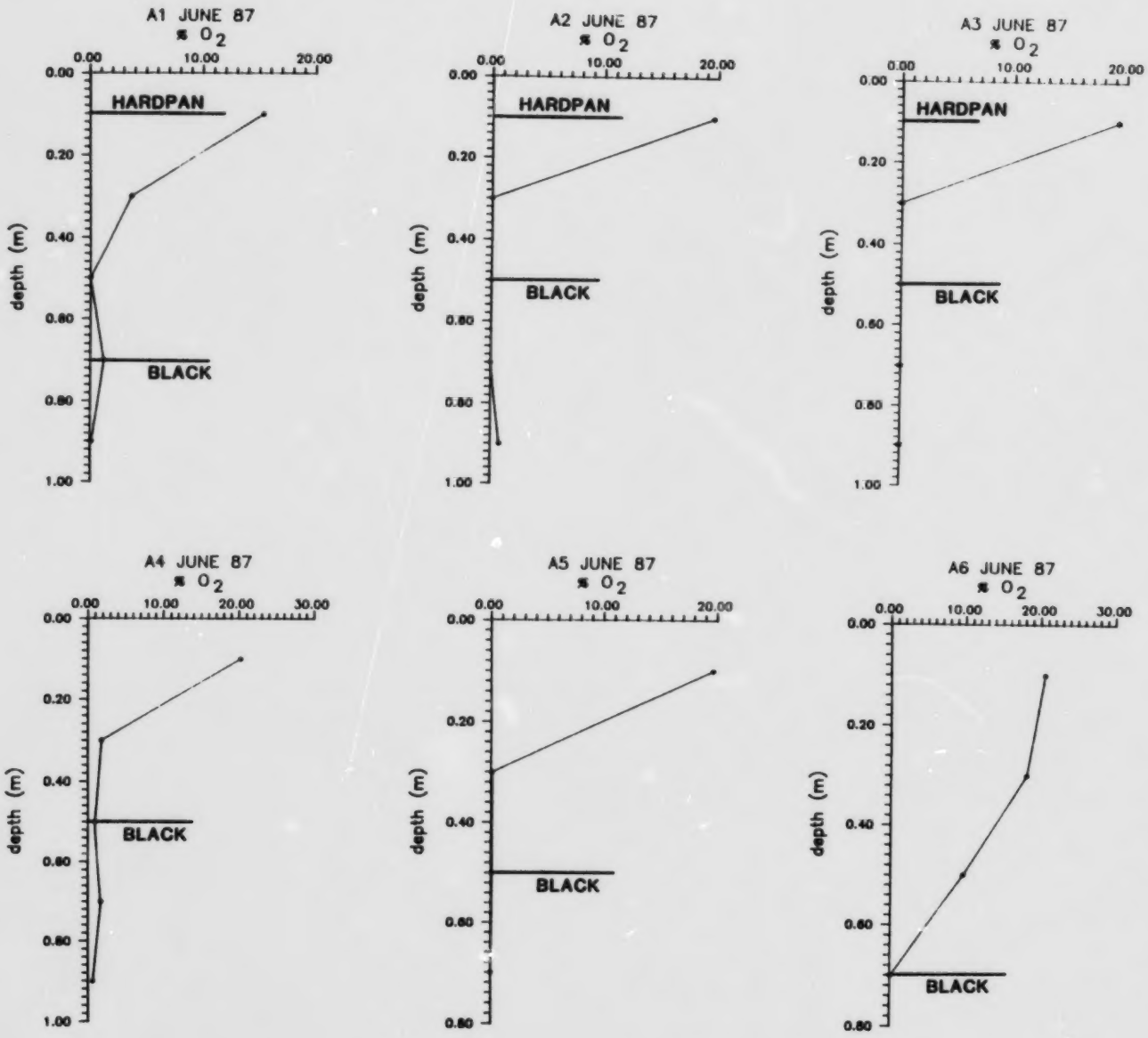


Figure C-1 - Pore Gas Oxygen, % O_2 - Stations A1-A6

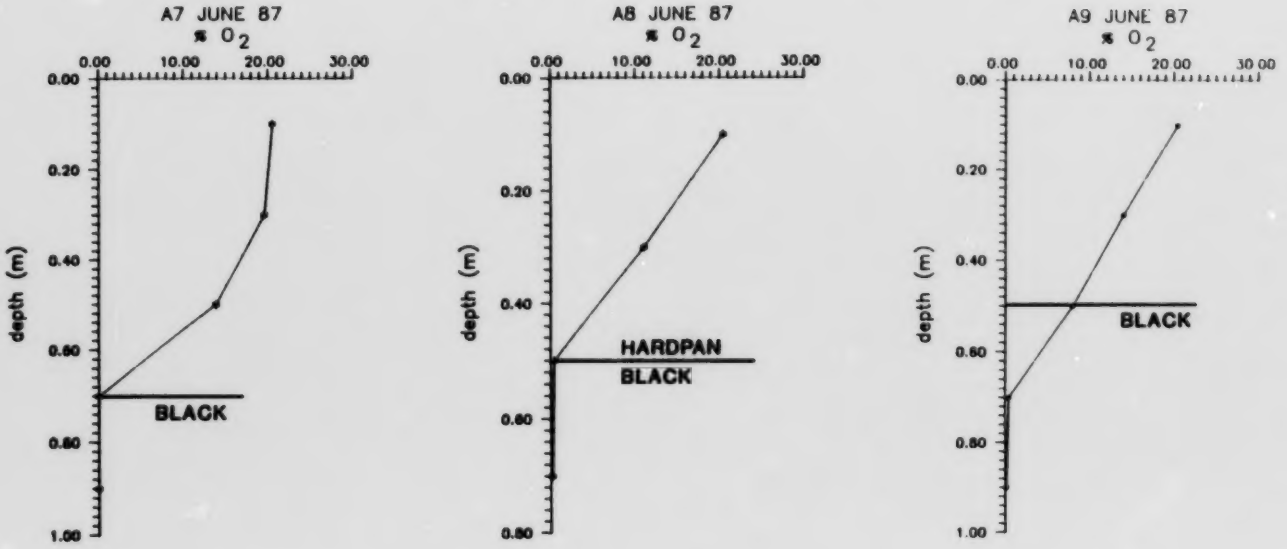


Figure C-2 - Pore Gas Oxygen, % O_2 - Stations A7-A9

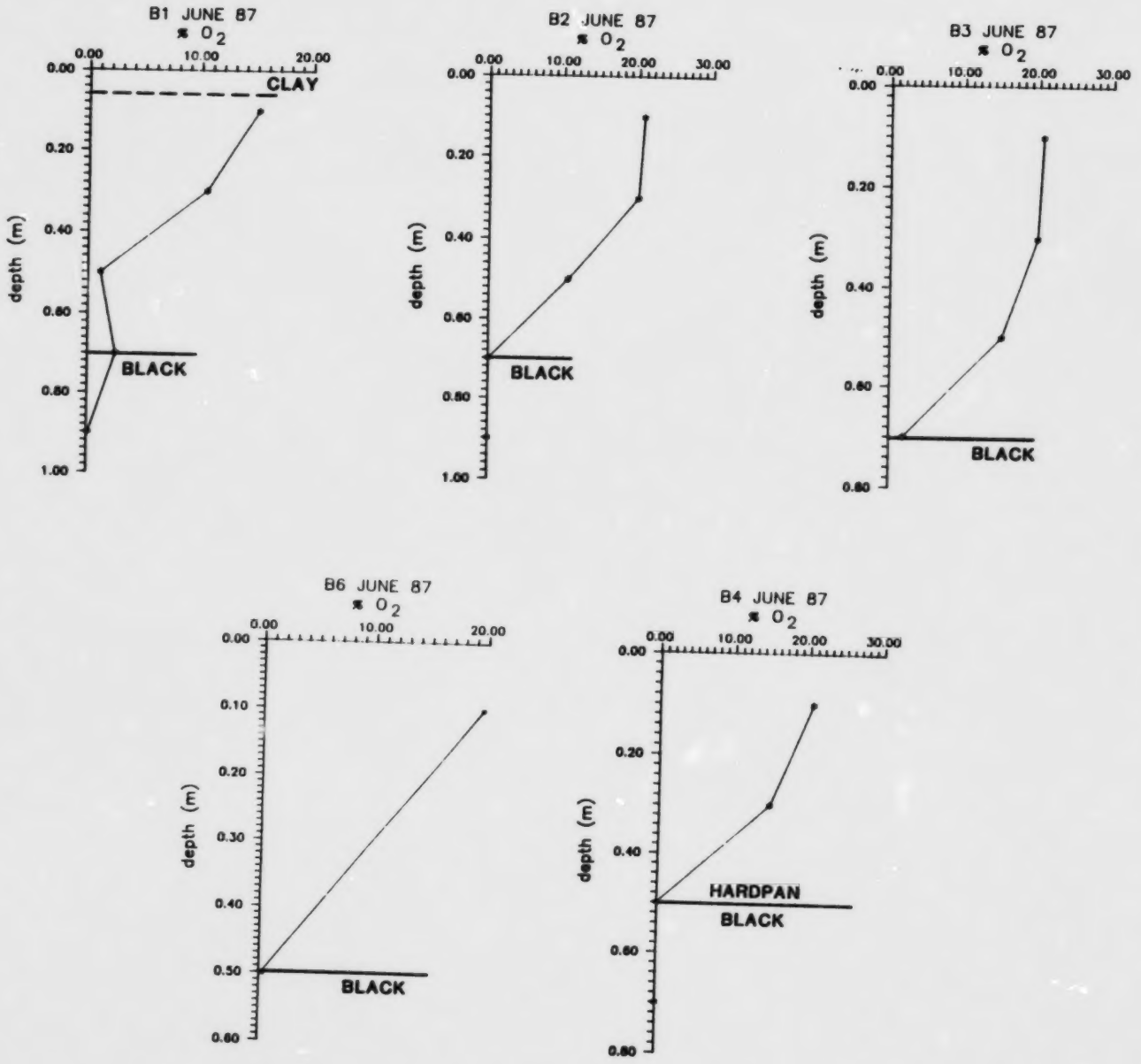


Figure C-3 - Pore Gas Oxygen, % O_2 - Stations B1-B4, B6

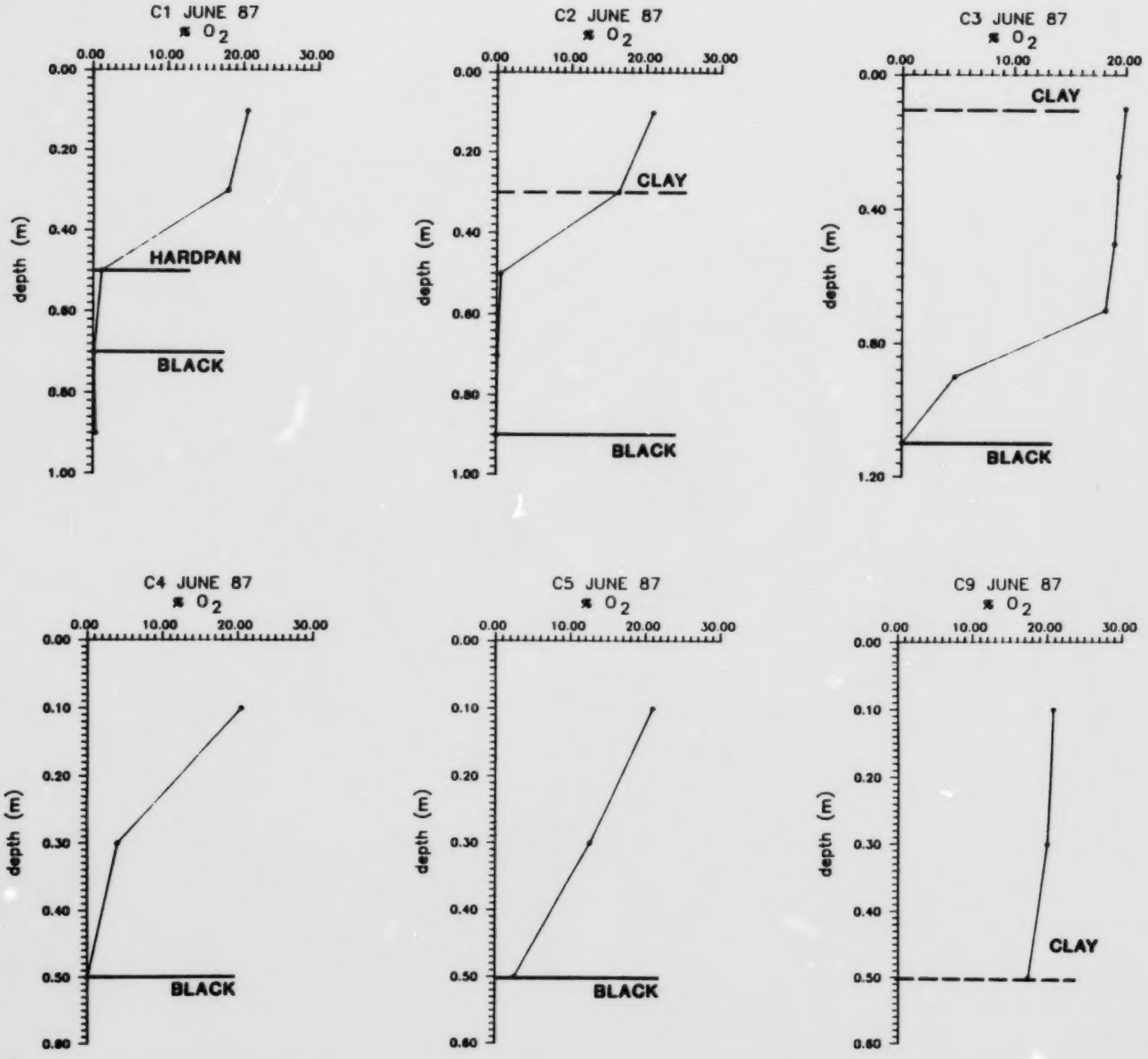


Figure C-4 - Pore Gas Oxygen, % O_2 - Stations C1-C5, C9

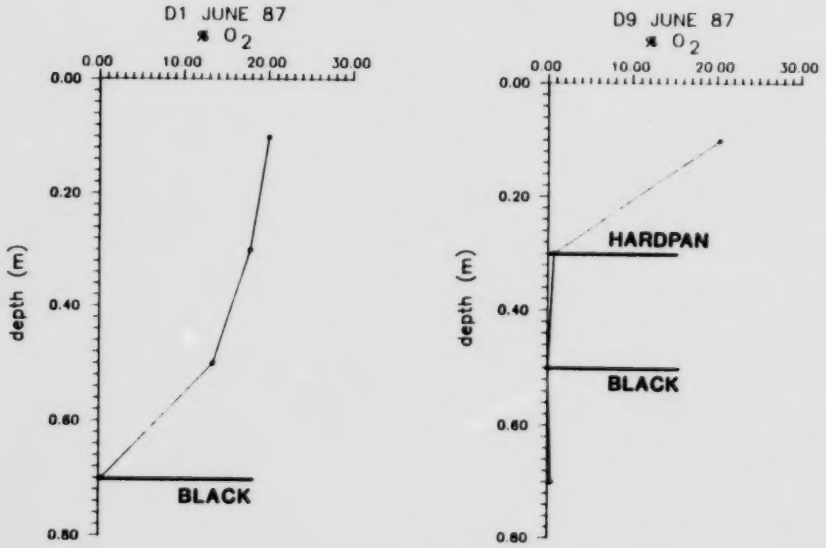


Figure C-5 - Pore Gas Oxygen, % O_2 - Stations D1, D9

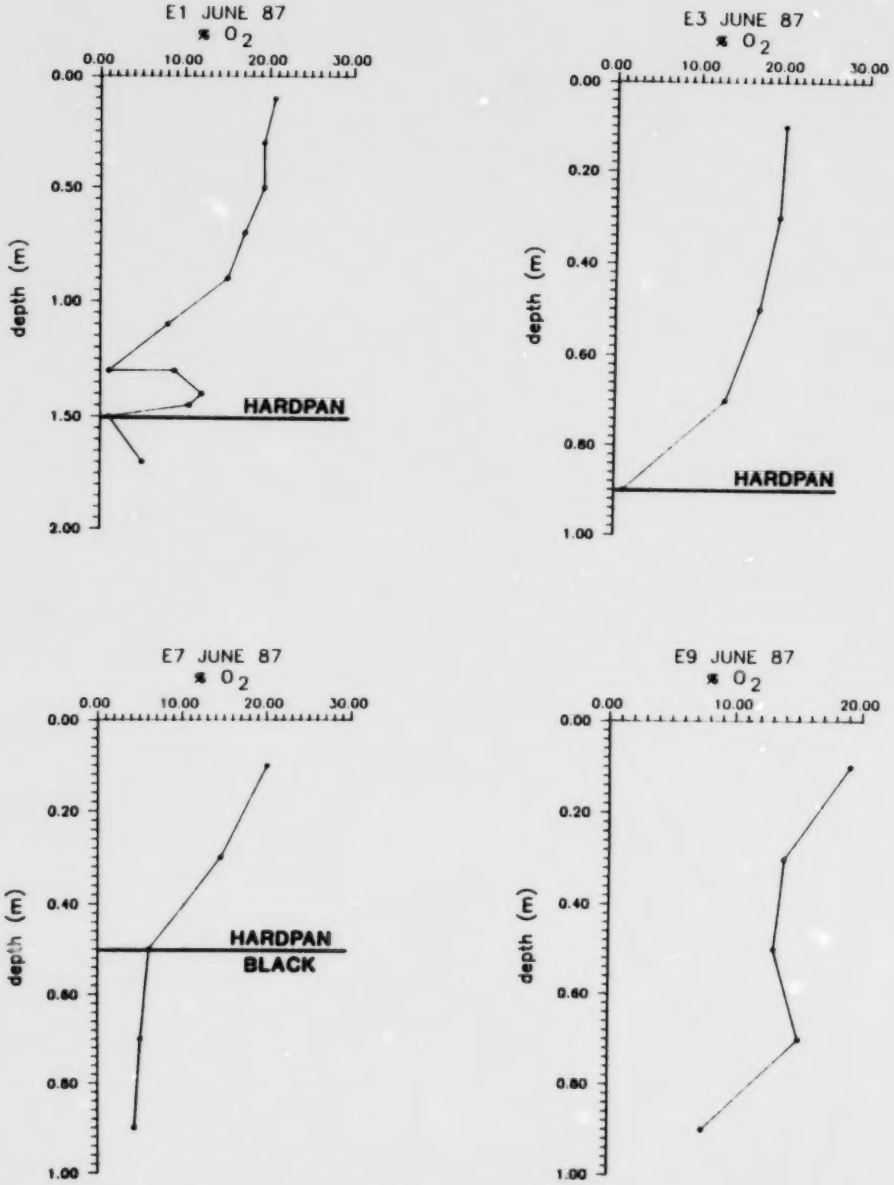


Figure C-6 - Pore Gas Oxygen, % O_2 - Stations E1, E3, E7, E9

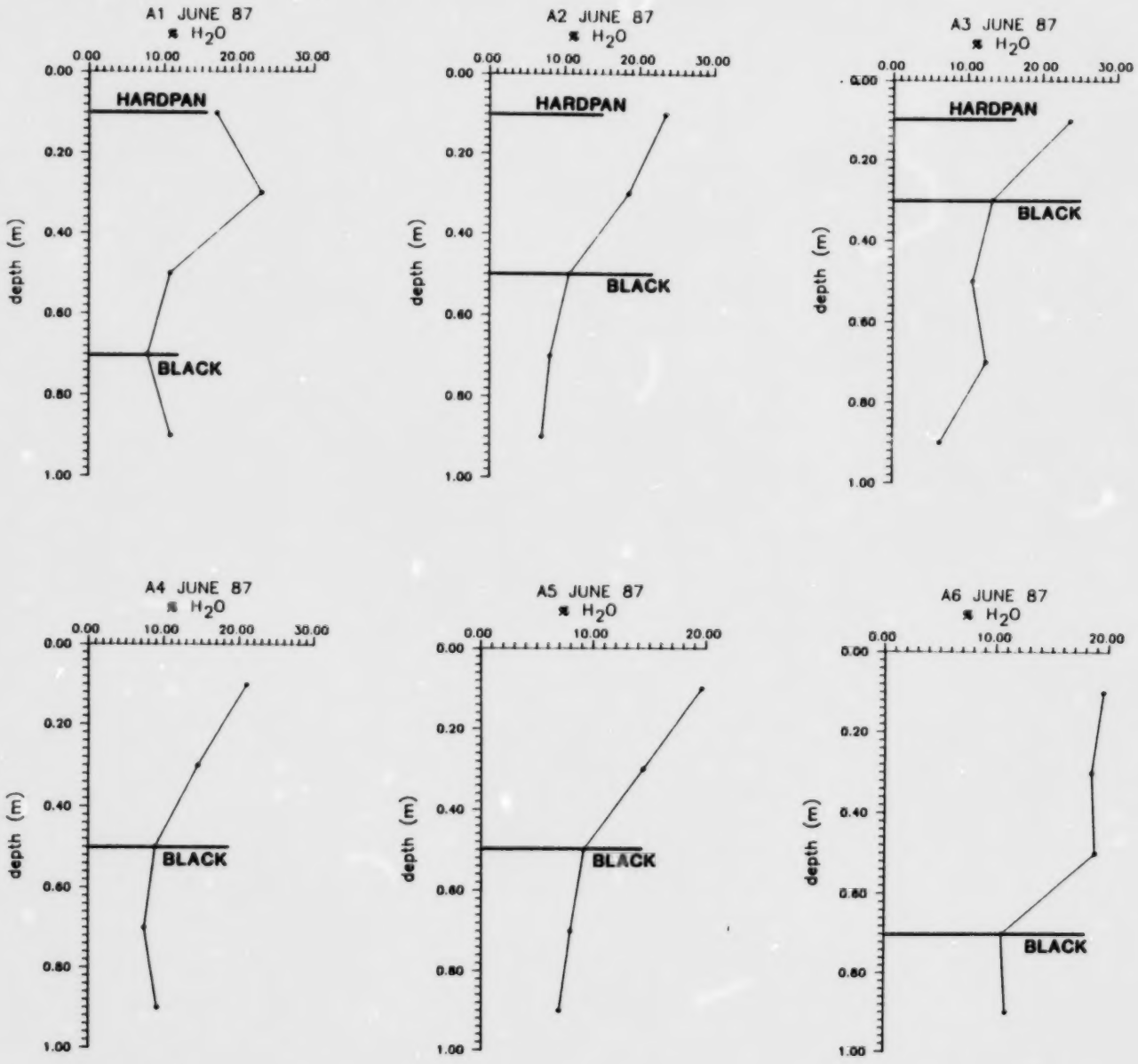


Figure C-7 - Pore Gas Oxygen, % H_2O - Stations A1-A6

APPENDIX D

PROFILES OF TAILINGS % MOISTURE AT PORE GAS SAMPLING POINTS

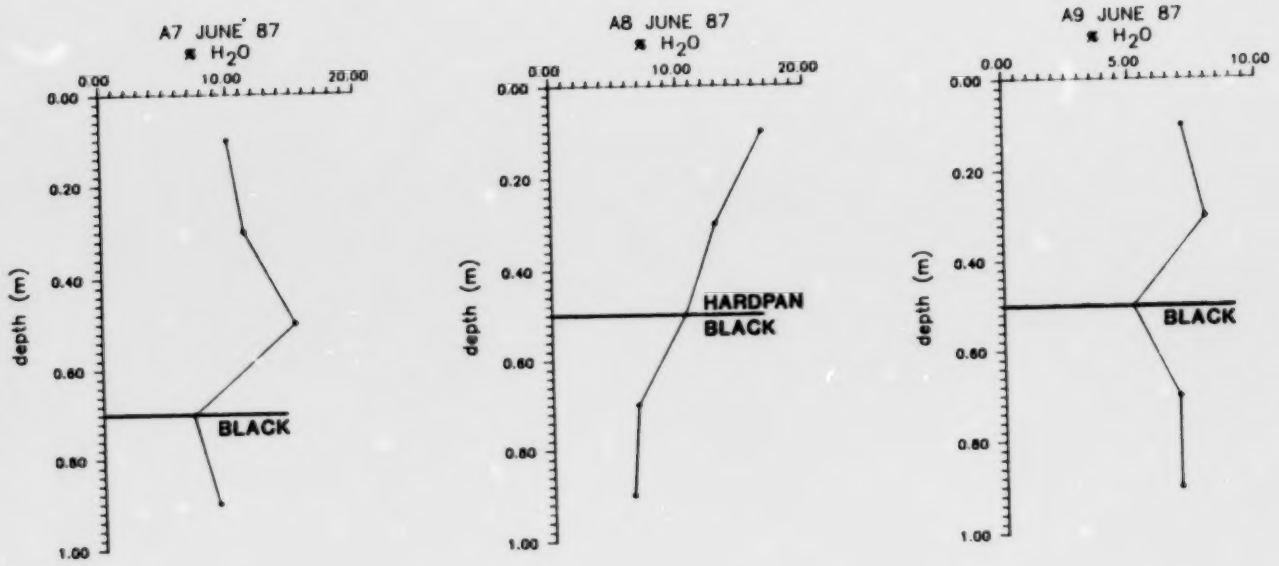


Figure D-1 - Tailings % Moisture, Stations A7-A9

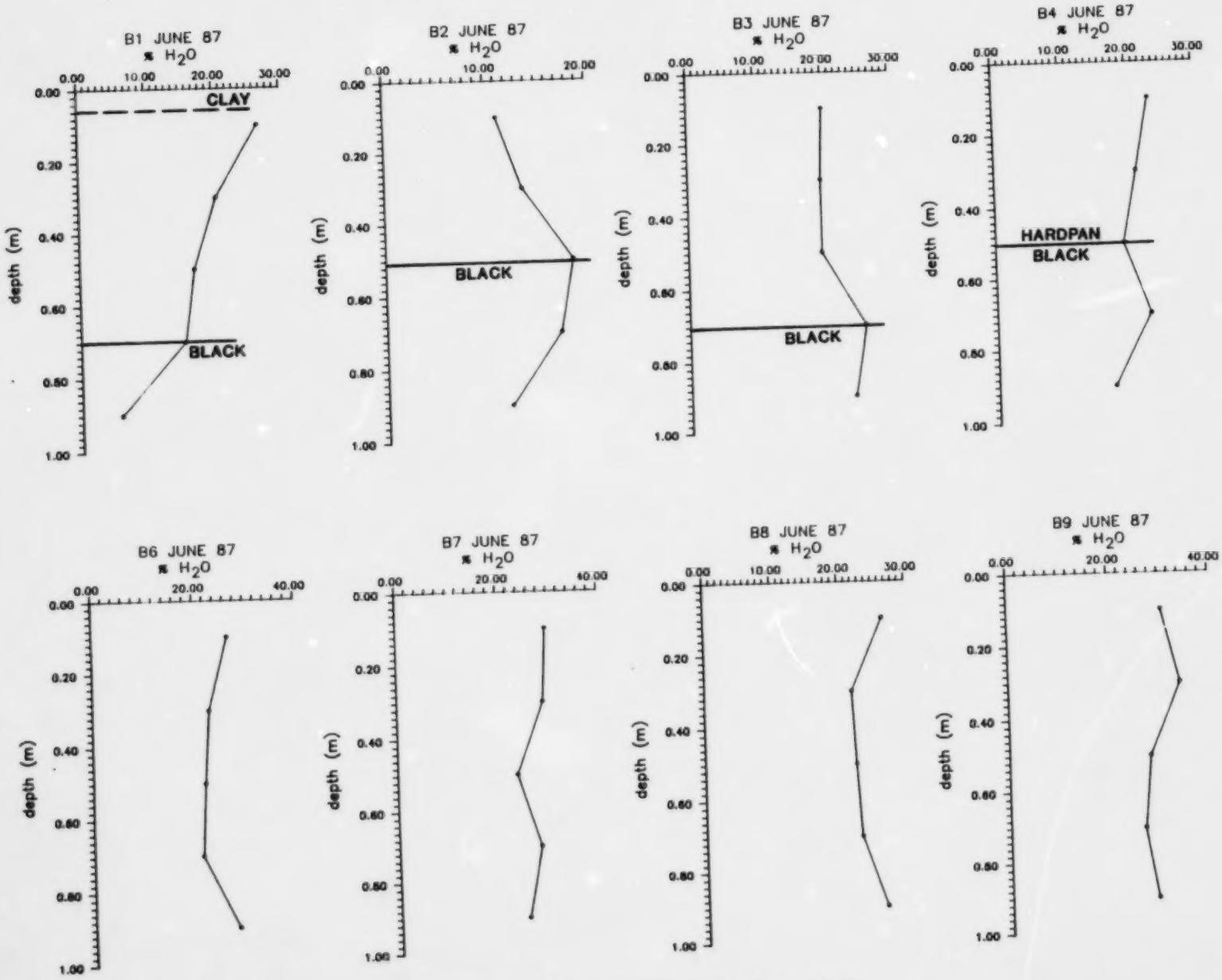


Figure D-2 - Tailings % Moisture, B1-B4, B6-B9

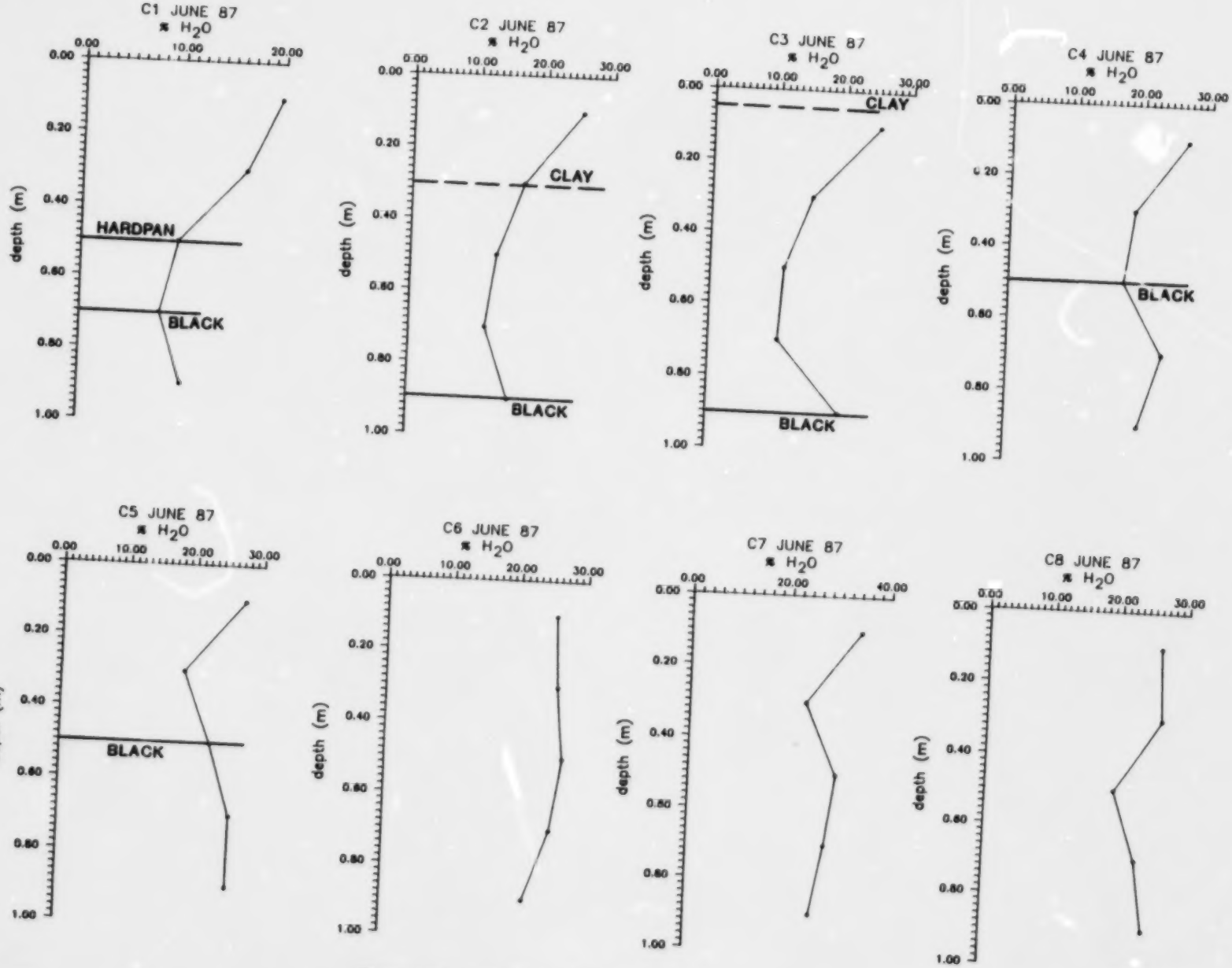


Figure D-3 - Tailings % Moisture, Stations C1-C8

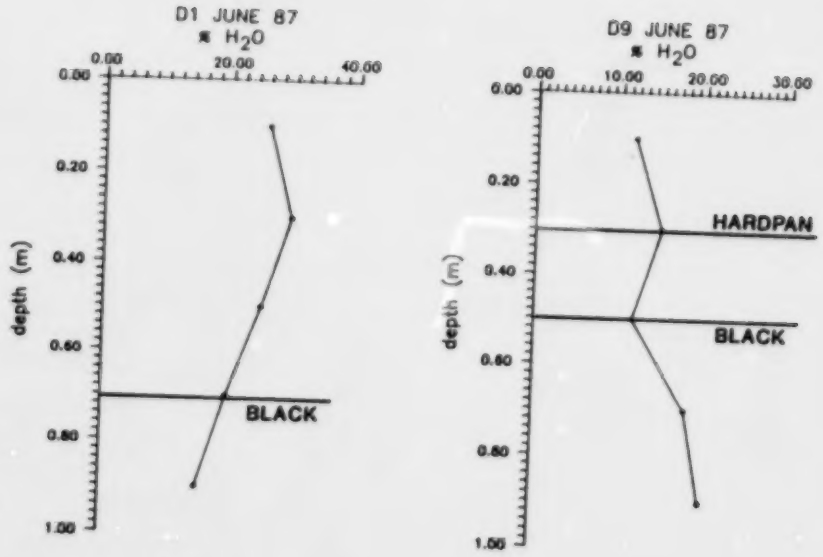


Figure D-4 - Tailings % Moisture, Stations D1, D9

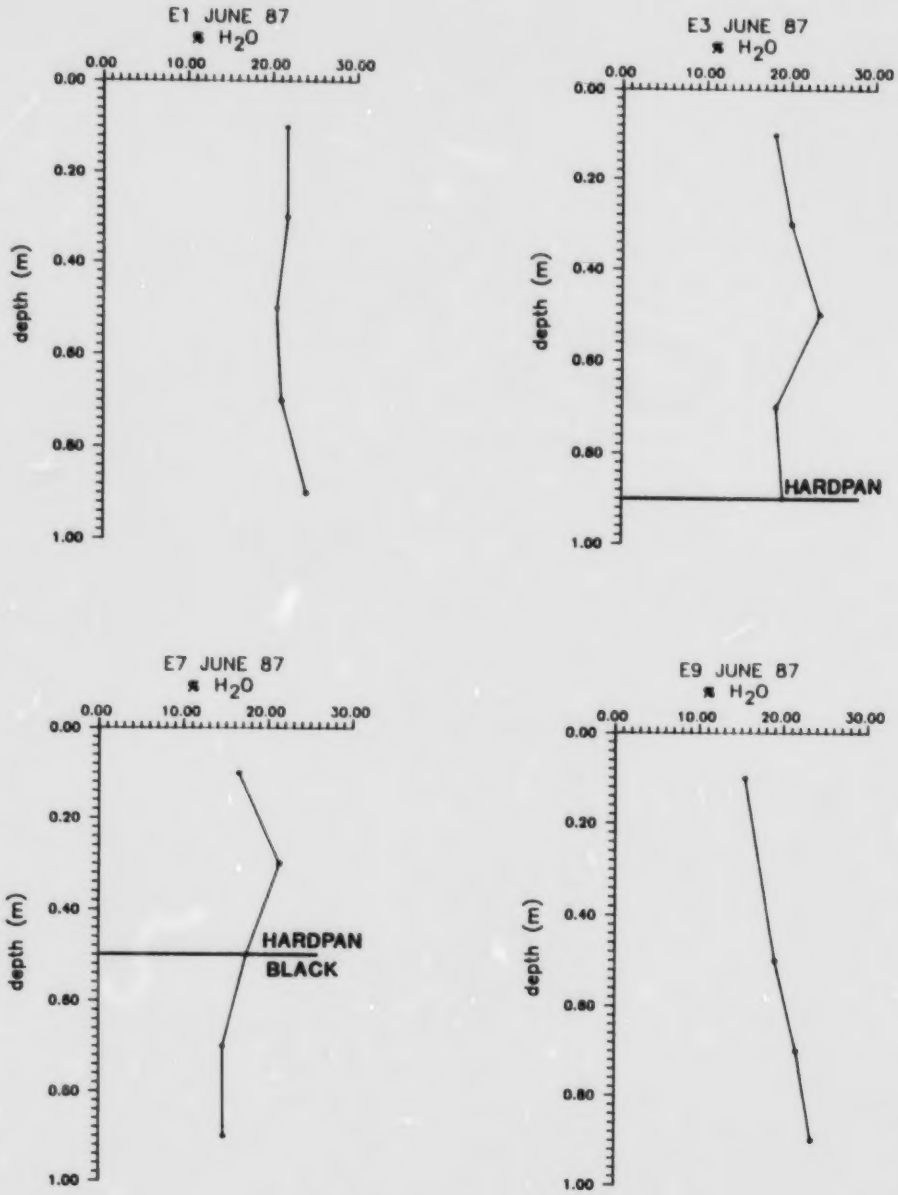


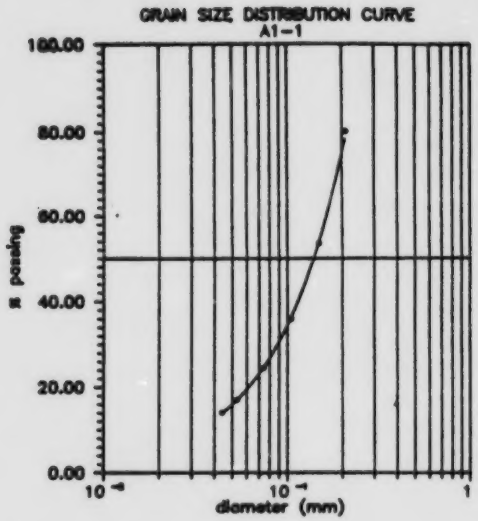
Figure D-5 - Tailings % Moisture, Stations E1, E3, E7, E9

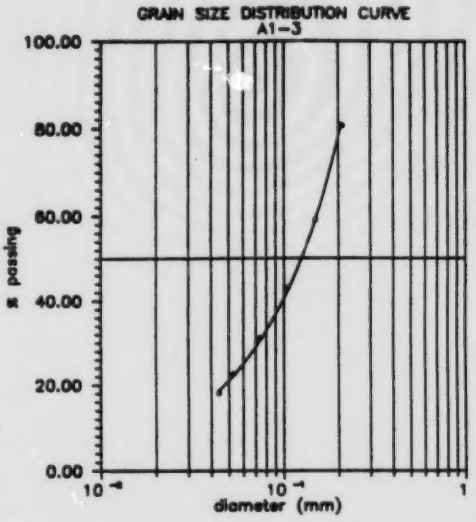
APPENDIX E

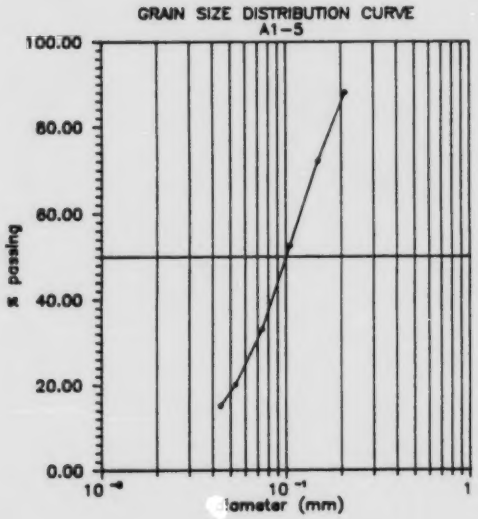
GRAIN SIZE DISTRIBUTION AND SUMMARY OF OXYGEN PROFILES, TAILINGS GRAIN SIZES, MOISTURE CONTENT AND FIELD OBSERVATIONS

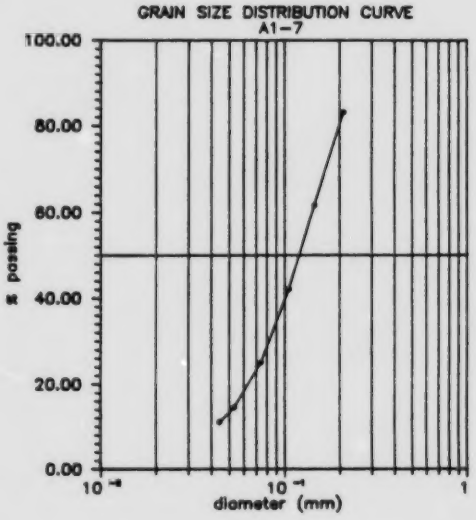
- Figure E-1 to E-12 - Grain Size Distribution

- Table E-I - Oxygen Profiles, Tailings Grain Size and Moisture Content, and Field Observations









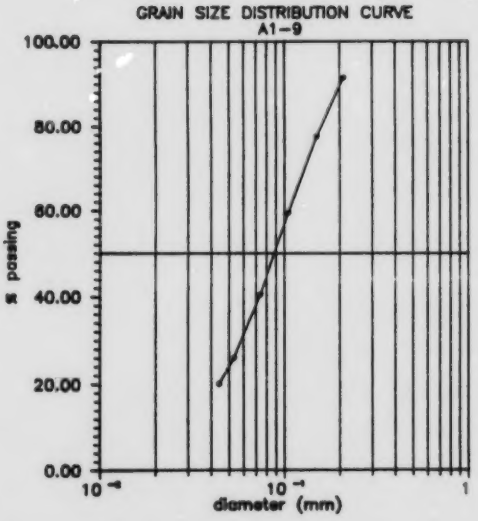
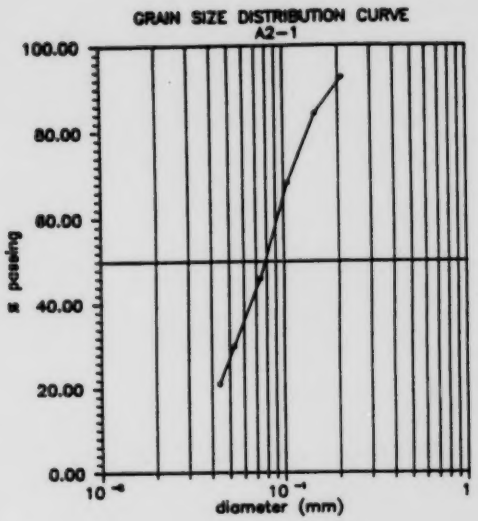
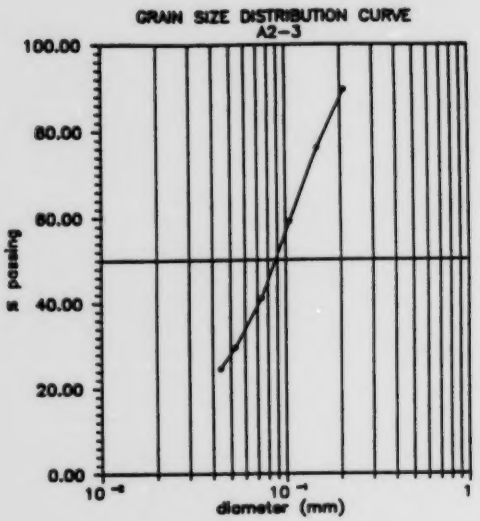
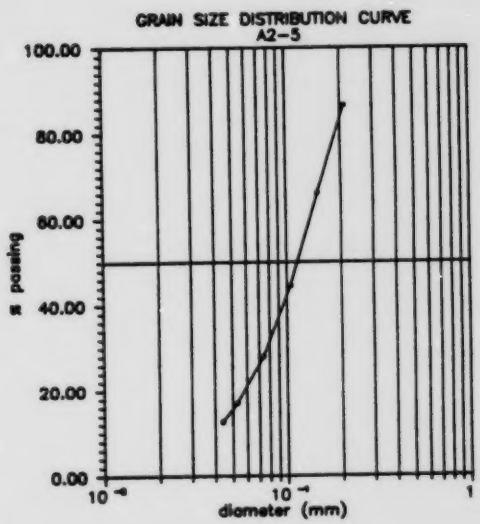
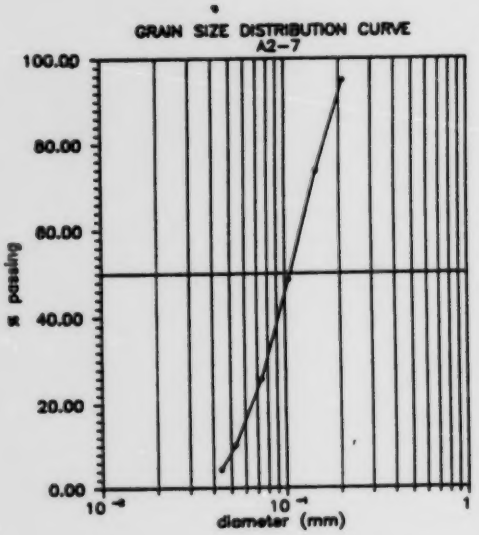


Figure E-1 - Size Distribution, Station A1









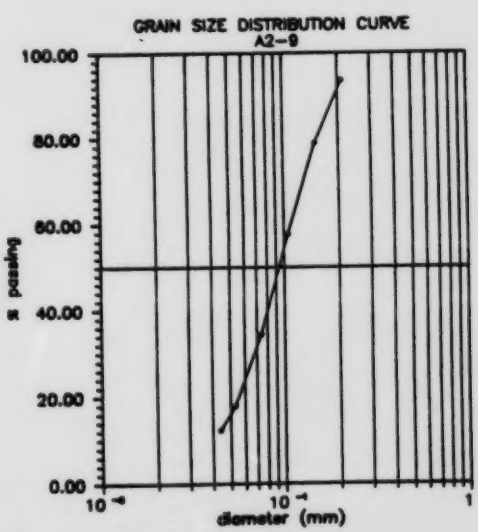
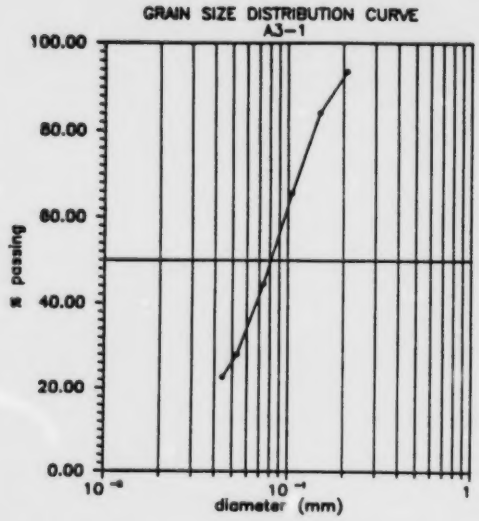
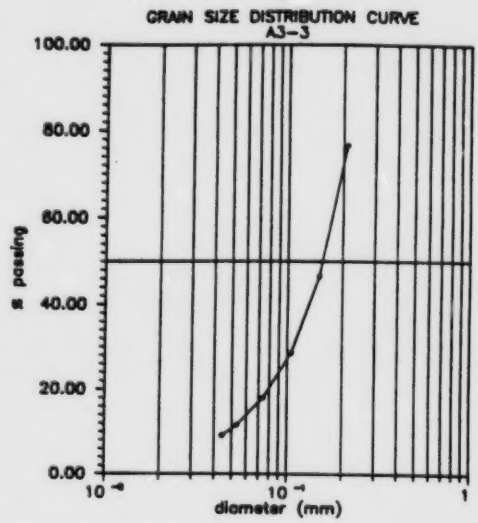
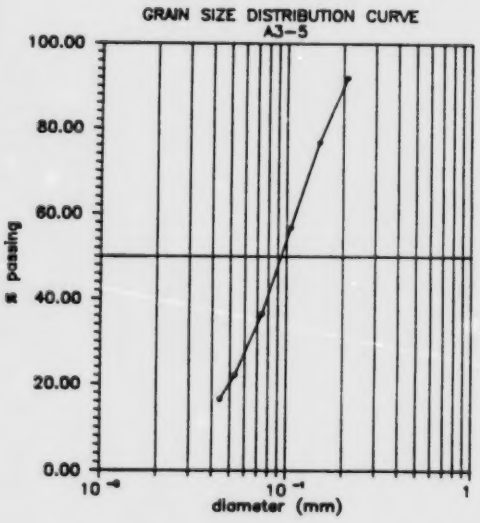
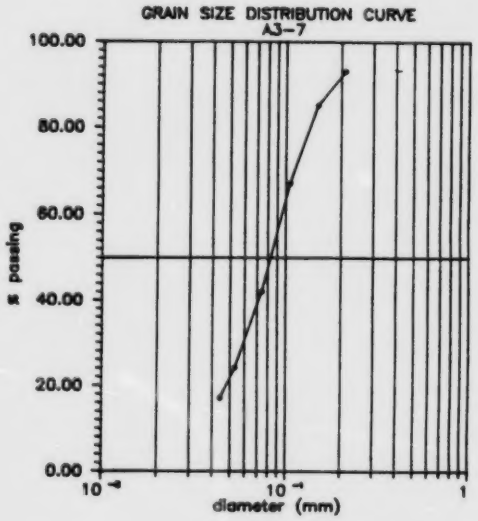


Figure E-2 - Size Distribution, Station A2









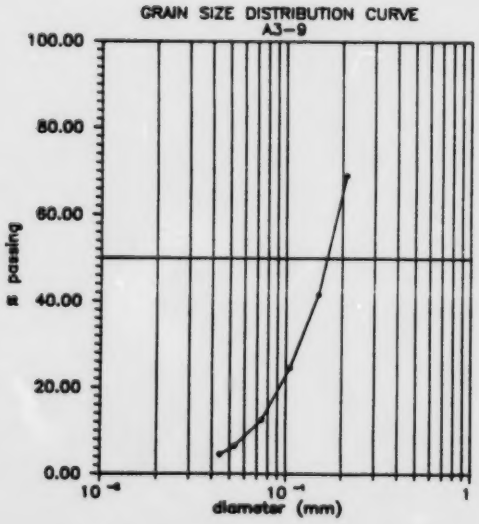


Figure E-3 - Size Distribution, Station A3

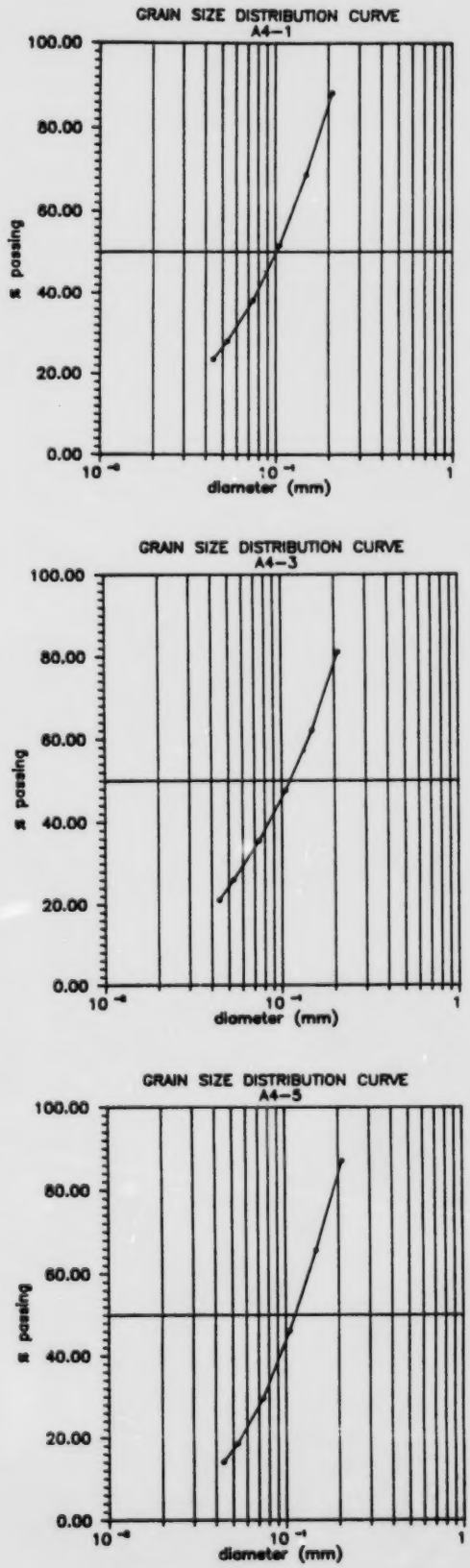
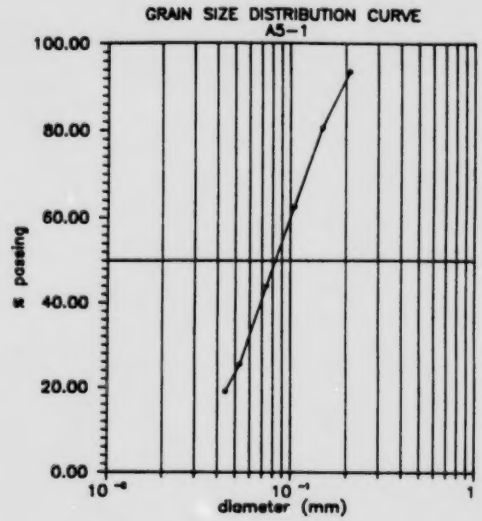
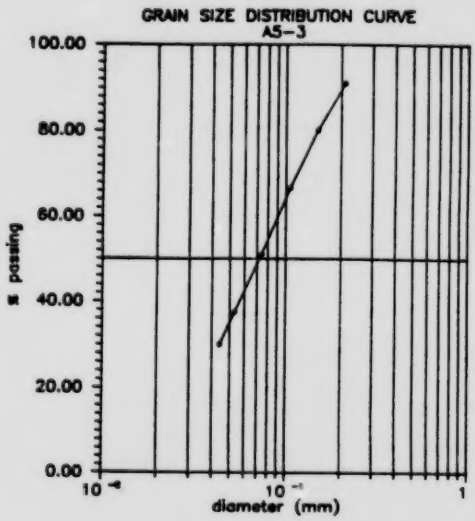
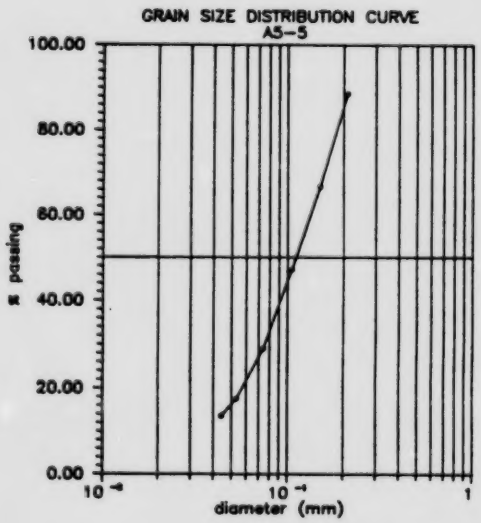


Figure E-4 - Size Distribution, Station A4







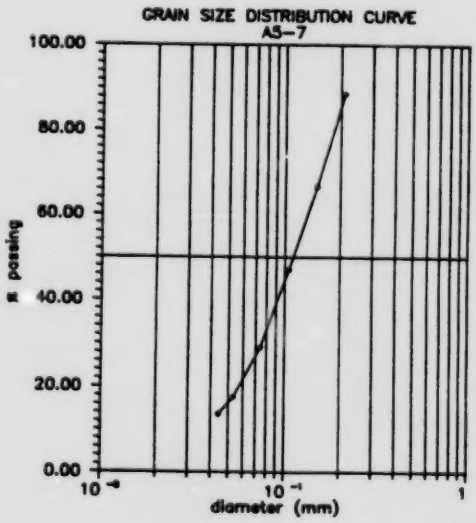
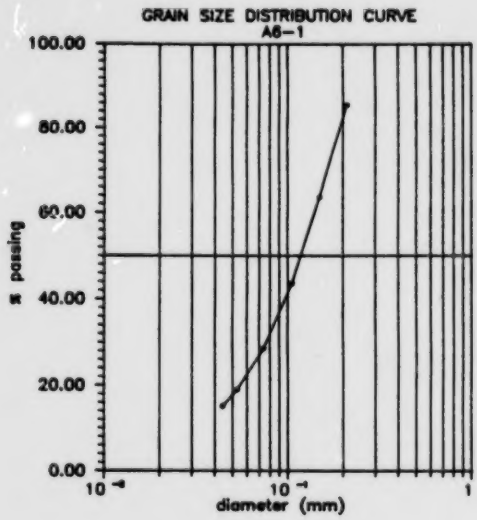


Figure E-5 - Size Distribution, Station A5



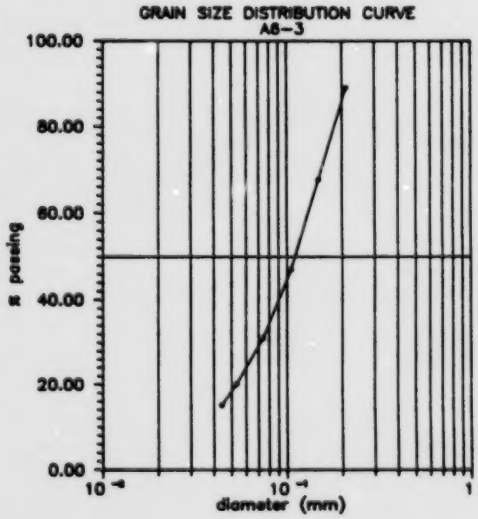
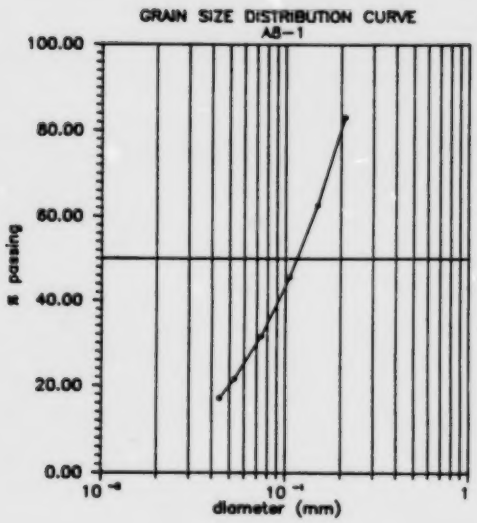


Figure E-6 - Size Distribution, Station A6



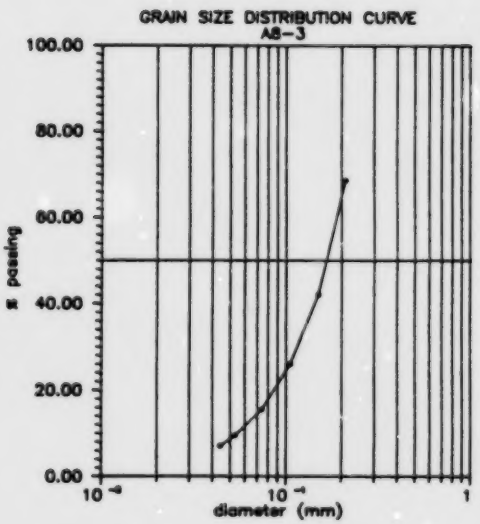
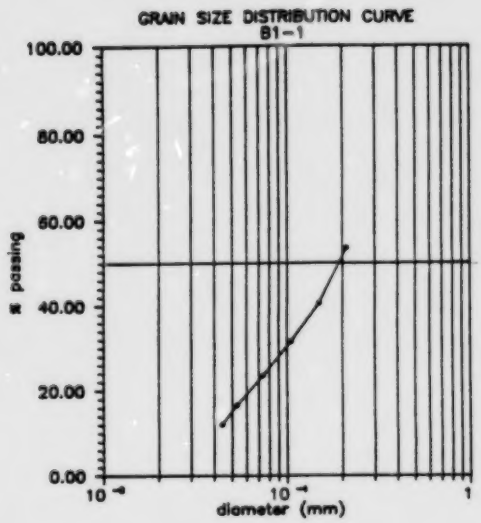
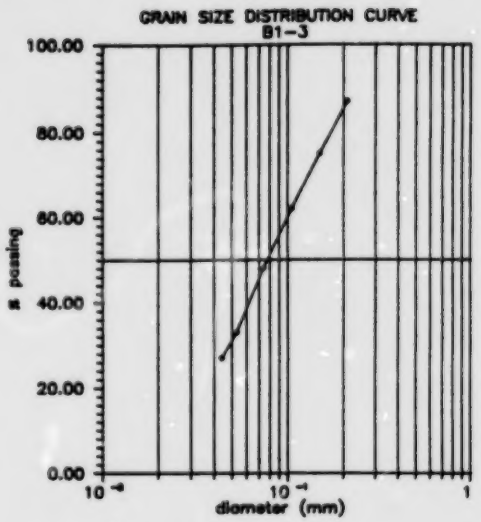
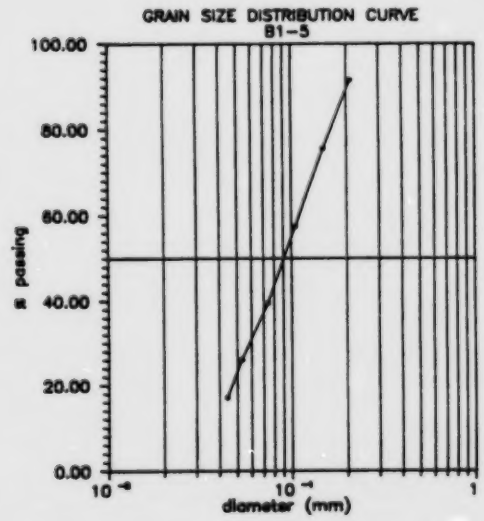
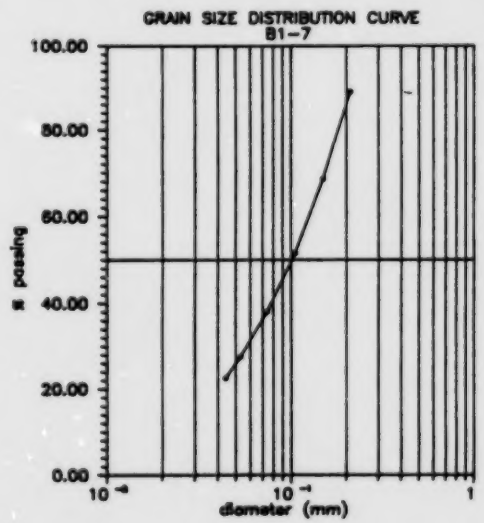


Figure E-7 - Size Distribution, Station A8









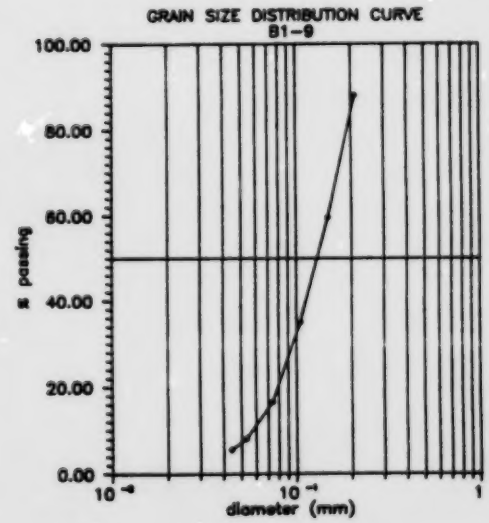
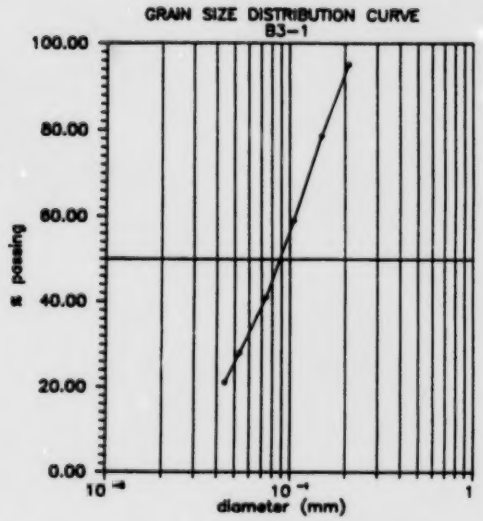
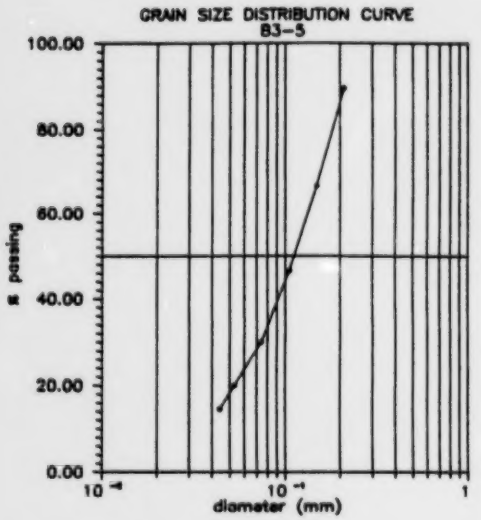
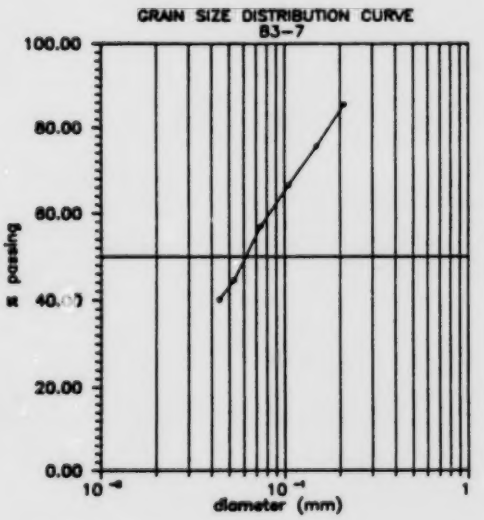


Figure E-8 - Size Distribution, Station B1







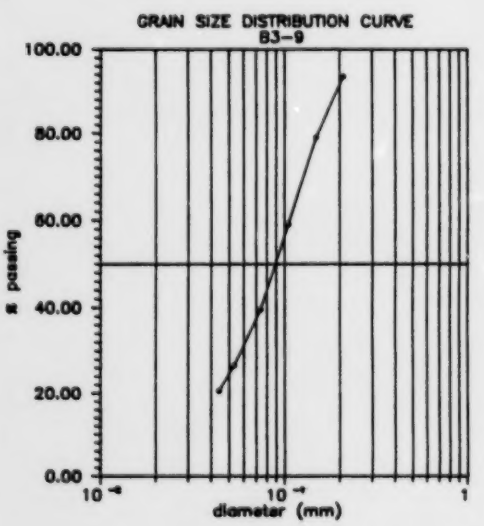
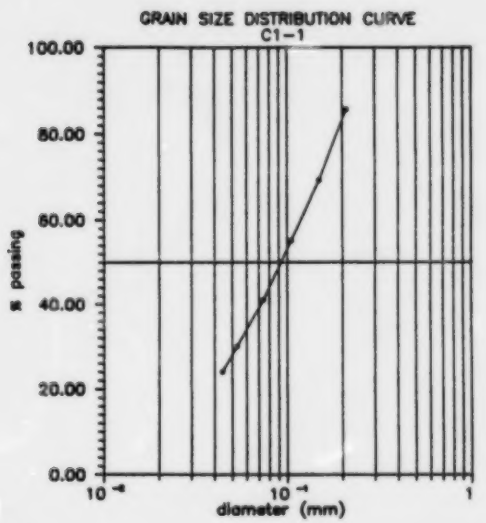
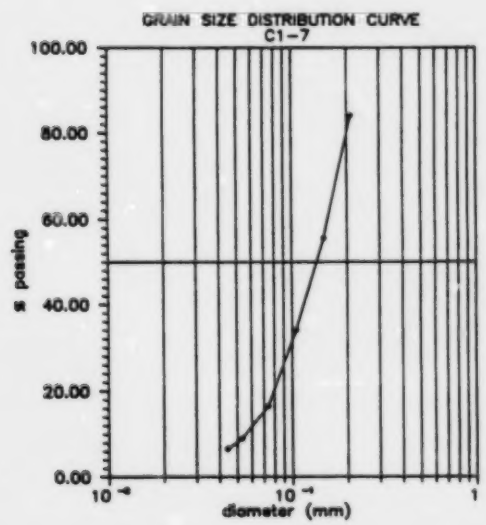


Figure E-9 - Size Distribution, Station B3





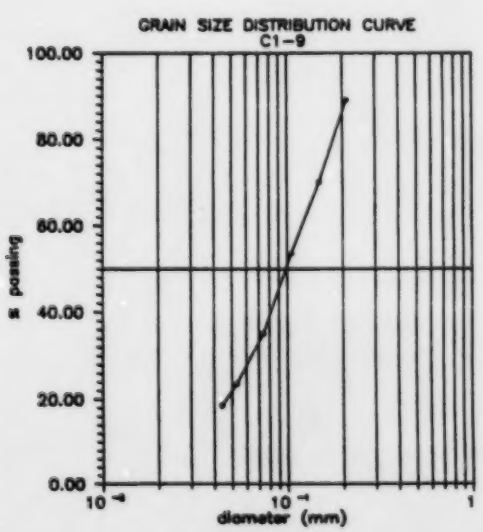
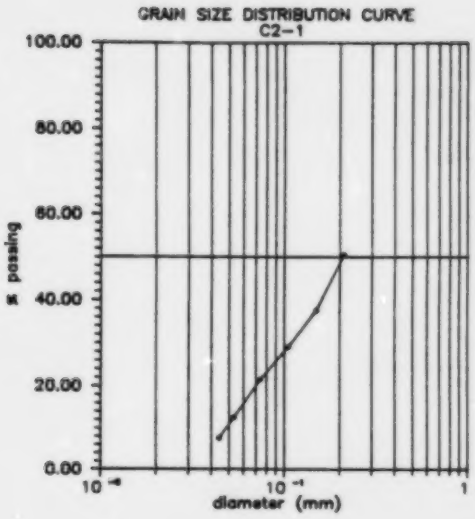


Figure E-10 - Size Distribution, Station C1



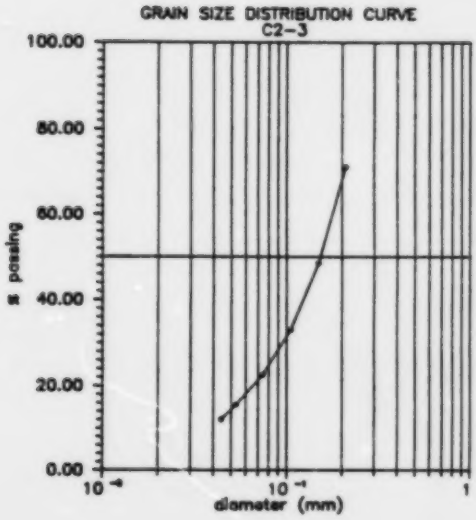
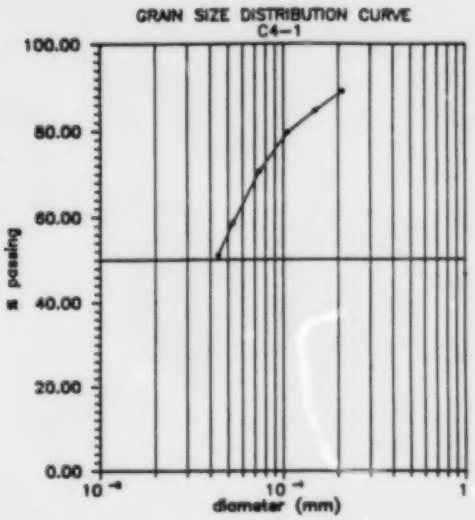
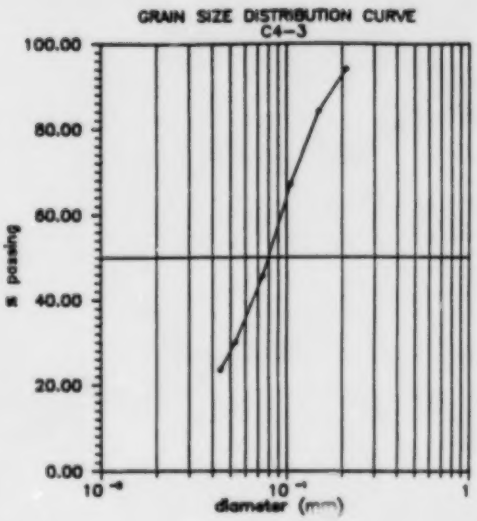
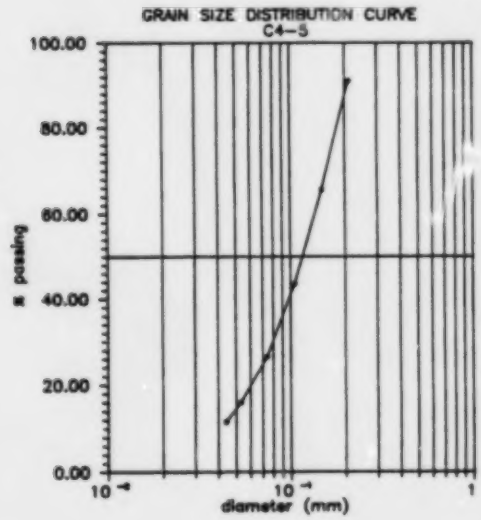
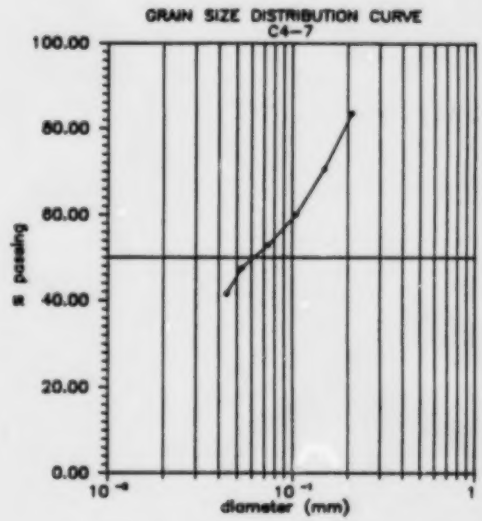


Figure E-11 - Size Distribution, Station C2









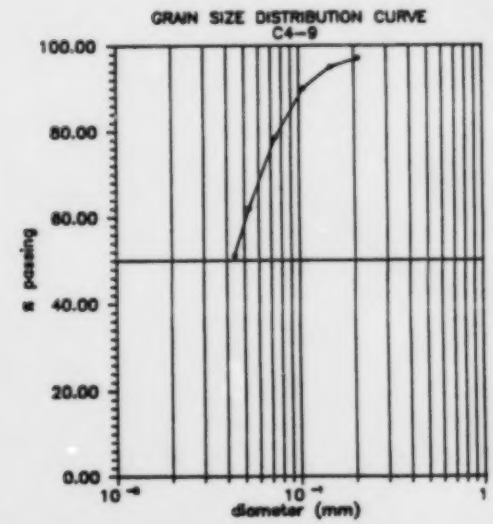
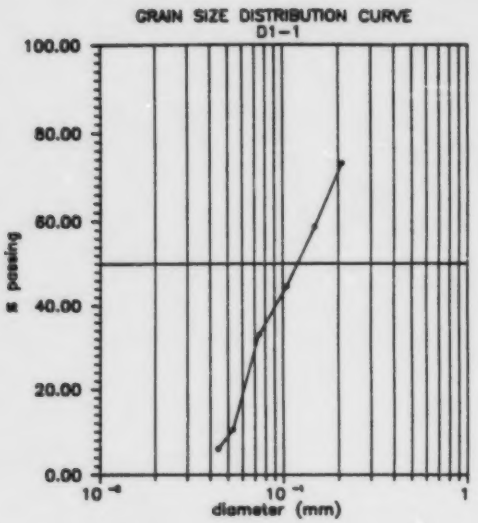
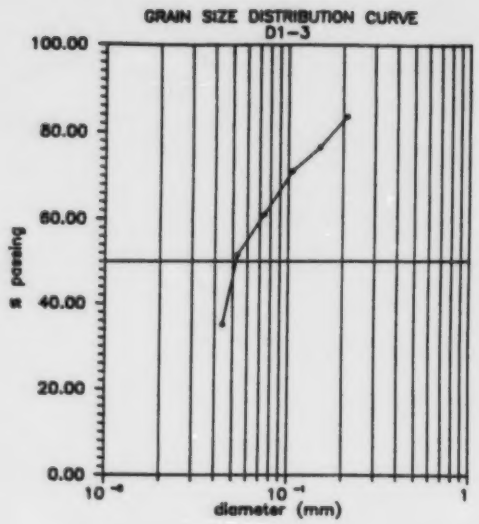
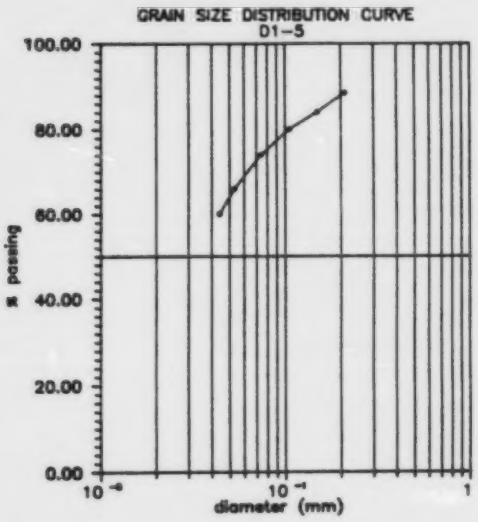
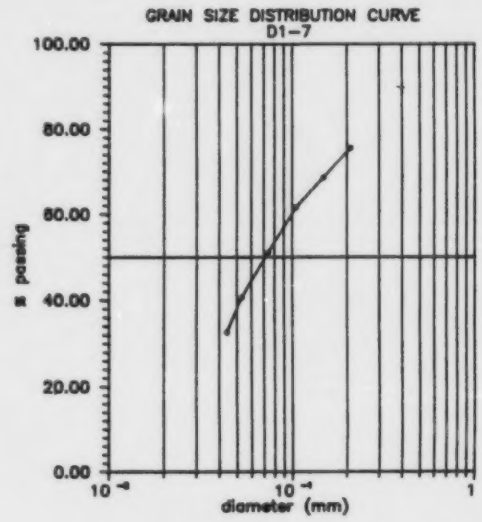


Figure E-12 - Size Distribution, Station C4









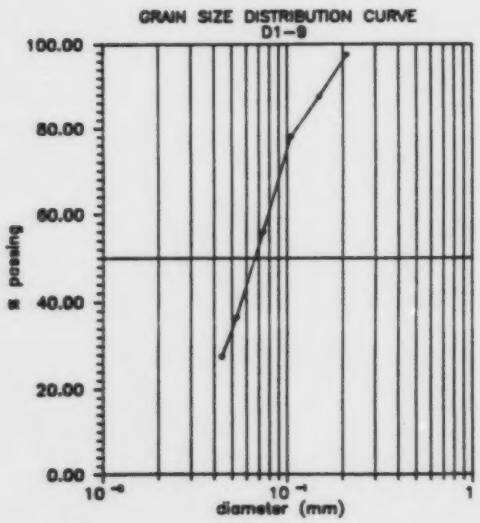
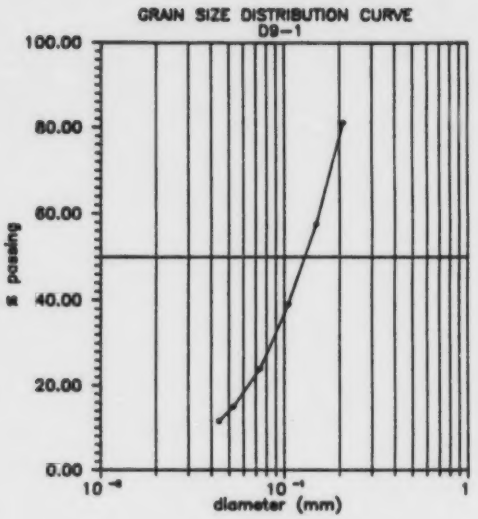


Figure E-13 - Size Distribution, Station D1



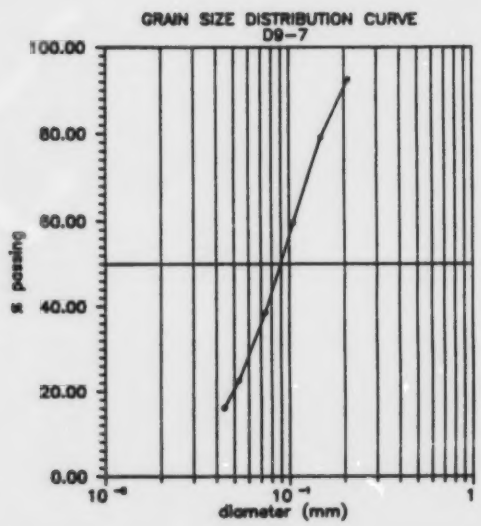
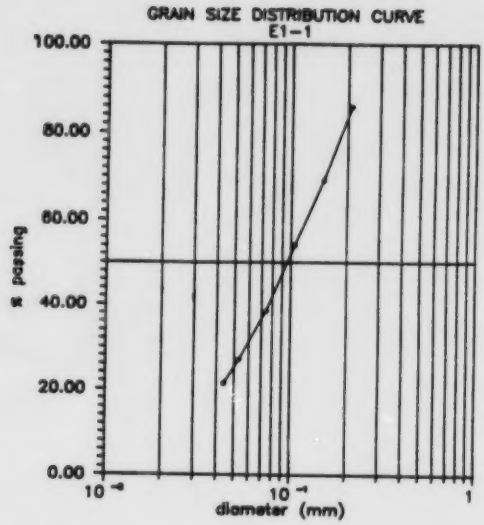
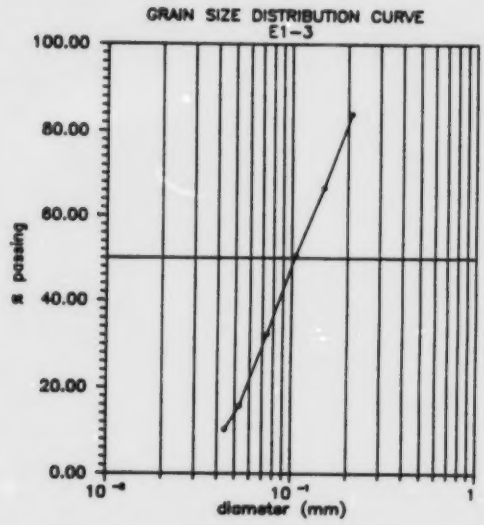


Figure E-14 - Size Distribution, Station D9





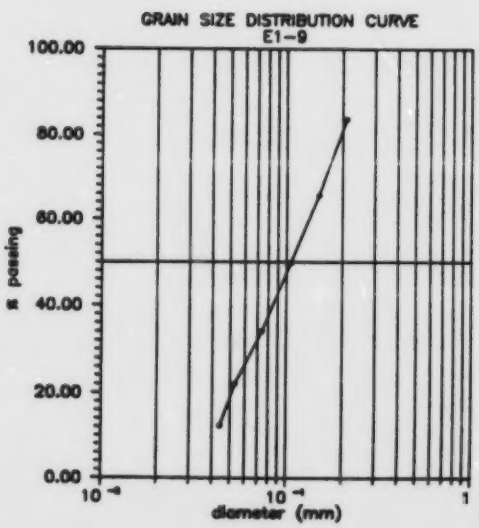
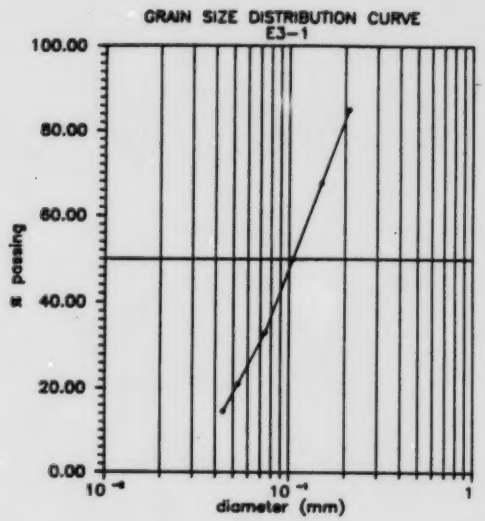
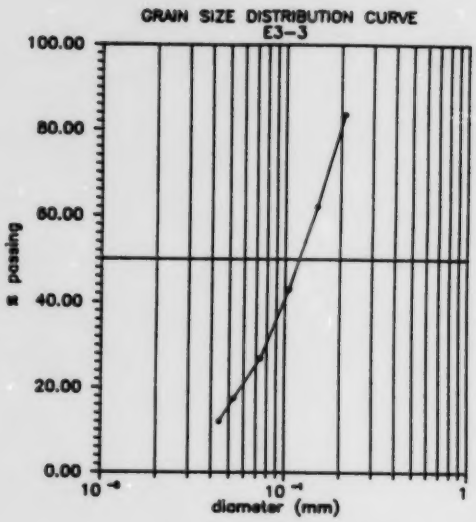
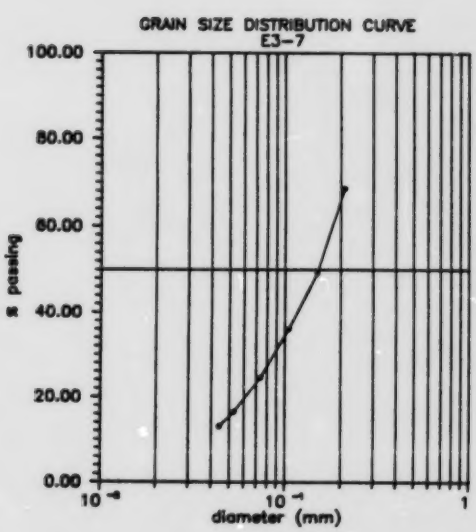


Figure E-15 - Size Distribution, Station E1







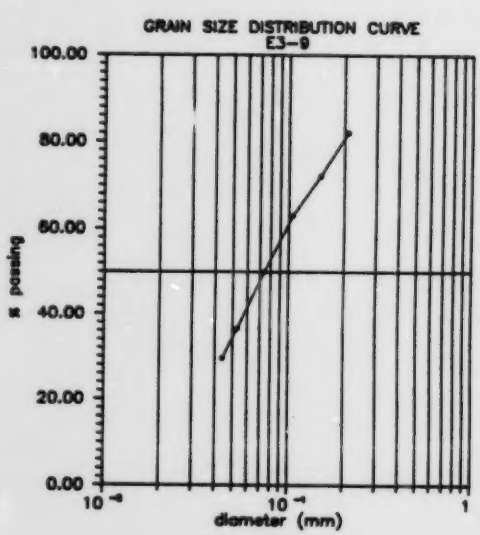
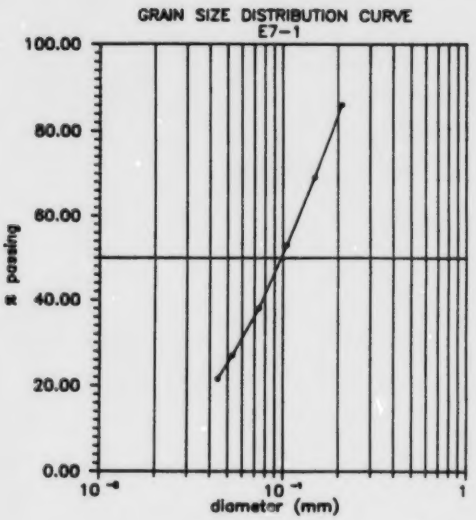
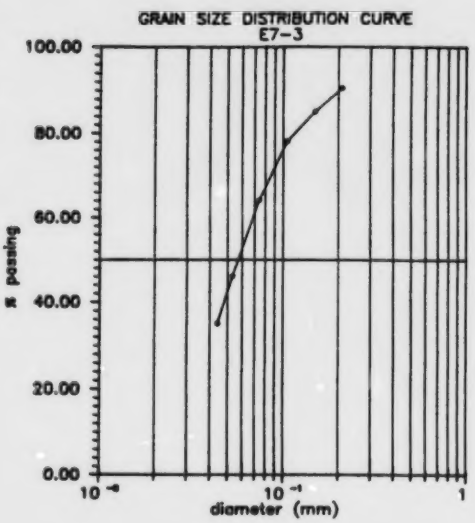
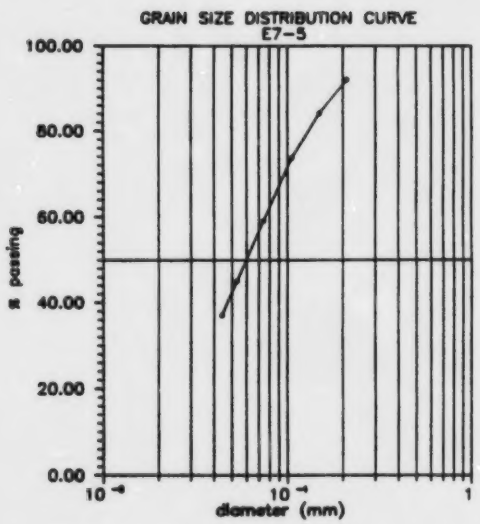


Figure E-16 - Size Distribution, Station E3







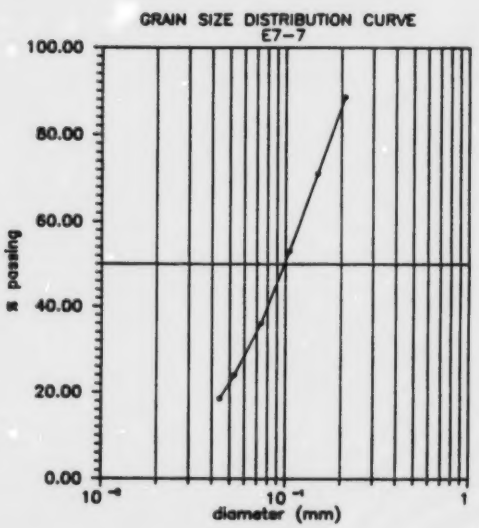
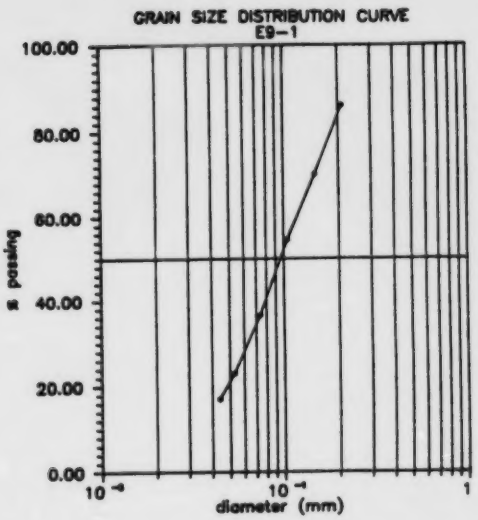
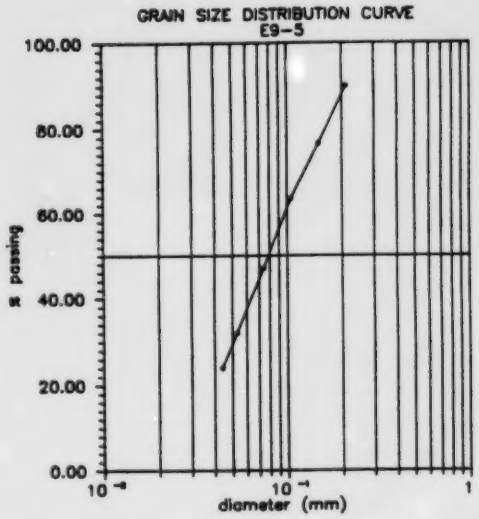
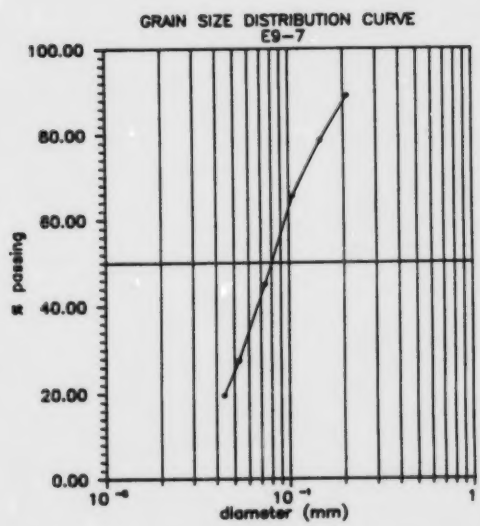


Figure E-17 - Size Distribution, Station E7







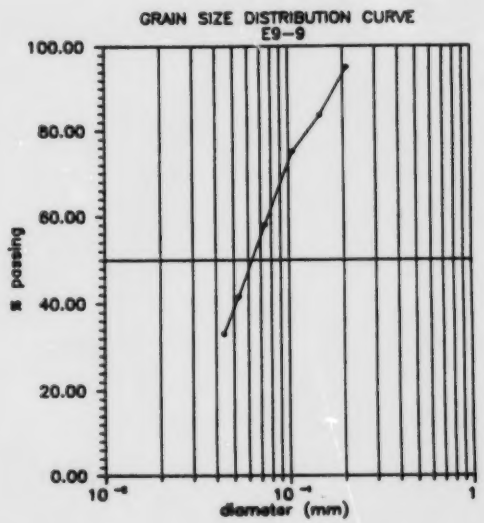


Figure E-18 - Size Distribution, Station E9

TABLE E-I (p. 1 of 5)

OXYGEN PROFILES, TAILINGS GRAIN SIZE AND MOISTURE CONTENT, AND FIELD OBSERVATIONS

Date Sampled	Station	Depth (m)	O_2 (%)	H_2O (%)	d_{50} (microns)	Colour	Depth to Hard Pan (m)	Cover	Clay Covered
03-06-87	A1	0.1	15.3	17.0	104	reddish	0.1	vegetated	no
		0.3	3.6	23.0	103	reddish			
		0.5	0.0	10.8	100	reddish, black, some grey			
		0.7	1.2	7.8	102	black			
		0.9	0.1	10.9	88	black			
04-06-87	A2	0.1	19.6	23.4	79	reddish	0.1	vegetated	no
		0.3	0.0	8.5	88	reddish, black			
		0.5	0.0	10.5	102	black, some grey			
		0.7	0.0	8.0	101	black			
		0.9	0.8	6.9	93	black			
04-06-87	A3	0.1	19.3	23.6	80	reddish	0.1	vegetated	no
		0.3	0.0	13.2	106	reddish, some grey			
		0.5	0.0	10.6	94	black			
		0.7	0.0	12.4	82	black			
		0.9	0.0	6.3	107	black			
04-06-87	A4	0.1	20.2	21.0	100	reddish		vegetated	no
		0.3	1.8	14.5	102	reddish			
		0.5	0.9	8.8	102	reddish, black			
		0.7	1.7	7.4		black			
		0.9	0.6	9.1		black			
12-06-87	A5	0.1	19.6	19.6	84	reddish		vegetated	no
		0.3	0.1	14.4	72	reddish, greenish-black			
		0.5	0.1	9.1	101	black, greenish			
		0.7	0.0	7.9	101	black, greenish			
		0.9	-	6.9		black, greenish			
16-06-87	A6	0.1	20.5	19.5	102	reddish		vegetated	no
		0.3	18.0	18.4	101	reddish			
		0.5	9.7	18.7		layering of grey and red			
		0.7	0.1	10.4		black			
		0.9	-	10.8		black			
22-07-87	A7	0.1	20.5	10.0		reddish		vegetated	no
		0.3	19.5	11.2		reddish			
		0.5	13.8	15.2		reddish-black			
		0.7	0.0	7.1		black			
		0.9	0.0	9.0		black			

TABLE E-I (p. 2 of 5)

OXYGEN PROFILES, TAILINGS GRAIN SIZE AND MOISTURE CONTENT, AND FIELD OBSERVATIONS

Date Sampled	Station	Depth (m)	O_2 (%)	H_2O (%)	d_{50} (microns)	Colour	Depth to Hard Pan (m)	Cover	Clay Covered
16-06-87	A8	0.1	20.4	16.7	102	reddish		vegetated	no
		0.3	11.0	12.9	107	reddish	0.5-0.55		
		0.5	0.4	10.5	107	reddish-black			
		0.7	0.2	6.7	-	black			
		0.9	-	6.3	-	black			
22-08-87	A9	0.1	20.4	7.1		reddish		vegetated	no
		0.3	14.0	8.0		reddish-black			
		0.5	8.0	5.1		black			
		0.7	0.4	6.9		black			
		0.9	0.1	6.9		black			
12-06-87	B1	0.1	15.1	26.6	109	grey, reddish		vegetated	yes
		0.3	10.5	20.3	78	reddish, green			
		0.5	1.1	16.9	90	reddish, green			
		0.7	2.5	15.4	100	reddish, green-black			
		0.9	0.1	5.8	103	black			
05-08-87	B2	0.1	20.7	11.2		reddish		vegetated	no
		0.3	19.9	13.6		reddish			
		0.5	10.6	18.5		reddish, greenish, some clay			
		0.7	0.0	17.2		greenish-black			
		0.9	0.0	12.2		black			
	B3	0.1	20.5	20.1	88	reddish		vegetated	no
		0.3	19.7	19.7	88	reddish, greenish			
		0.5	15.0	19.7	101	reddish, greenish			
		0.7	1.9	26.1	62	reddish, greenish, brown, black			
		0.9	-	24.4	90	black			
05-08-87	B4	0.1	20.5	23.3		reddish, grey	0.5	vegetated	no
		0.3	14.8	21.1		reddish, grey-red			
		0.5	0.0	19.0		black			
		0.7	0.0	22.9		black			
		0.9	-	17.3		black			
18-08-87	B5	0.1	20.6			reddish, some grey	0.39	vegetated	no
		0.3	-			reddish-black			
		0.5	-			black			
		0.7	-			black			
		0.9	-			black			

TABLE E-I (p. 3 of 5)

OXYGEN PROFILES, TAILINGS GRAIN SIZE AND MOISTURE CONTENT, AND FIELD OBSERVATIONS

Date Sampled	Station	Depth (m)	O_2 (%)	H_2O (%)	d_{50} (microns)	Colour	Depth to Hard Pan (m)	Cover	Clay Covered
17-08-87	B6	0.1	19.6	26.8		brownish		vegetated	no
		0.3	-	23.0		brownish-black			
		0.5	0.2	22.1		black			
		0.7	-	21.4		black			
		0.9	-	28.3		black			
17-08-87	B7	0.1	20.5	29.6		brownish		vegetated	no
		0.3	18.5	28.8		brownish-black			
		0.5	0.4	23.6		black			
		0.7	-	28.1		black			
		0.9	-	25.3		black			
7-08-87	B8	0.1	20.6	26.5		brownish-black		tailings	no
		0.3	-	21.8		black			
		0.5	-	22.4		black			
		0.7	-	23.1		black			
		0.9	-	26.6		black			
17-08-87	B9	0.1	17.6	30.6		brownish		vegetated	no
		0.3	12.5	34.0		brownish-black			
		0.5	-	27.8		black			
		0.7	-	26.5		black			
		0.9	-	28.8		black			
19-06-87	C1	0.1	20.5	19.7	94	reddish, some grey	0.3	vegetated	no
		0.3	17.9	16.3	104	greyish-red	0.5		
		0.5	1.1	9.7	104	deep reddish & brown-black			
		0.7	0.1	8.0	104	brown-black			
		0.9	0.4	10.3	98	brown-black, black			
16-06-87	C2	0.1	20.8	25.4	111	grey			
		0.3	16.2	16.8	106	reddish-grey			
		0.5	0.5	12.9	106	reddish			
		0.9	0.0	15.2	106	reddish-black			
05-08-87	C3	0.1	19.9	25.0		grey		vegetated	yes
		0.3	19.3	15.1		reddish			
		0.5	18.9	11.1		reddish-greenish			
		0.7	18.1	10.4		greenish			
		0.9	4.7	20.0		greenish-black			
		1.1	0.0	-					

OXYGEN PROFILES, TAILINGS GRAIN SIZE AND MOISTURE CONTENT, AND FIELD OBSERVATIONS

Date Sampled	Station	Depth (m)	O_2 (%)	H_2O (%)	d_{50} (microns)	Colour	Depth to Hard Pan (m)	Cover	Clay Covered
17-06-87	C4	0.1	20.4	26.5		reddish, some green		vegetated	no
		0.3	4.0	18.7	80	reddish, greenish-black			
		0.5	0.0	17.3	102	black			
		0.7	-	23.5	62	black			
		0.9	-	20.1		black			
13-08-87	C5	0.1	20.9	27.3		reddish, grey		vegetated	no
		0.3	12.6	18.4		brownish			
		0.5	2.5	22.5		brownish-black			
		0.7	-	25.8		black			
		0.9	-	25.6		black			
13-08-87	C6	0.1	20.6	25.4		brownish		vegetated	no
		0.3	11.2	25.8		brownish-black			
		0.5	-	26.8		black			
		0.7	-	25.2		black			
		0.9	-	21.5		black			
13-08-87	C7	0.1	20.6	34.0		brownish		vegetated	no
		0.3	13.4	23.2		black			
		0.5	-	29.6		black			
		0.7	-	27.7		black			
		0.9	-	25.1		black			
13-08-87	C8	0.1	20.5	26.0		brownish, grey		vegetated	no
		0.3	-	26.3		black			
		0.5	-	19.4		black			
		0.7	-	23.0		black			
		0.9	-	24.5		black			
18-08-87	C9	0.1	20.7			grey			
		0.3	19.8			grey			
		0.5	17.2			brownish-grey			
		0.7	-			brownish			
		0.9	-			brownish, grey-black	0.1-0.25		

TABLE E-I (p. 5 of 5)

OXYGEN PROFILES, TAILINGS GRAIN SIZE AND MOISTURE CONTENT, AND FIELD OBSERVATIONS

Date Sampled	Station	Depth (m)	O_2 (%)	H_2O (%)	d_{50} (microns)	Colour	Depth to Hard Pan (m)	Cover	Clay Covered
18-08-87	D9	0.1	20.3	11.6	103	reddish			
		0.3	0.7	14.9	103	reddish, greenish	0.6		
		0.5	0.0	11.6	103	black			
		0.7	0.4	18.1	90	black			
		0.9	-	20.1	90	black		contains rain	
	D1	0.1	20.0	25.8	102	reddish, greyish			
		0.3	17.8	29.4	52	reddish, greyish			
		0.5	13.4	24.9		red, brown, green,grey, black			
		0.7	0.3	19.7	72	black			
		0.9	-	15.3	78	black			
	E1	0.1	20.6	21.7	101	reddish			
		0.3	19.3	21.7	101	reddish			
		0.5	19.3	20.4	101	reddish			
		0.7	17.0	21.0	101	reddish			
		0.9	15.0	24.0	101	reddish			
		1.1	8.0	-	-				
		1.3	1.0	-	-				
		1.3	8.8	-	-				
		1.4	12.0	-	-				
		1.45	10.5	-	-				
		1.5	1.0	-	-		1.5		
		1.7	1.5	-	-				
	E3	0.1	20.0	18.1	101	red			
		0.3	19.3	20.0	102	red			
		0.5	17.0	23.4	102	red, greyish			
		0.7	13.0	18.2	105	reddish			
		0.9	1.0	19.1	74	reddish, black	0.9		
	E7	0.1	20.0	16.5	96	reddish			
		0.3	14.5	21.3	58	black, grey, red			
		0.5	6.0	17.4	60	black	0.5-0.55		
		0.7	5.0	14.6	96	black			
		0.9	4.3	14.7	98	black			
	E9	0.1	19.0	15.4	94	green, brown, grey			
		0.3	13.8	-	-	green, brown, grey			
		0.5	13.0	19.0	78	black, reddish			
		0.7	15.0	21.6	80	black, reddish			
		0.9	7.4	23.4	63	black, reddish			

APPENDIX F

JUNE 1987 SAMPLING PROGRAM PROFILES OF CHEMICAL/PHYSICAL CHARACTERISTICS OF PORE WATER (Ec, Eh, pH, acidity, Fe_T, Zn Ca, Mg, SO_4)

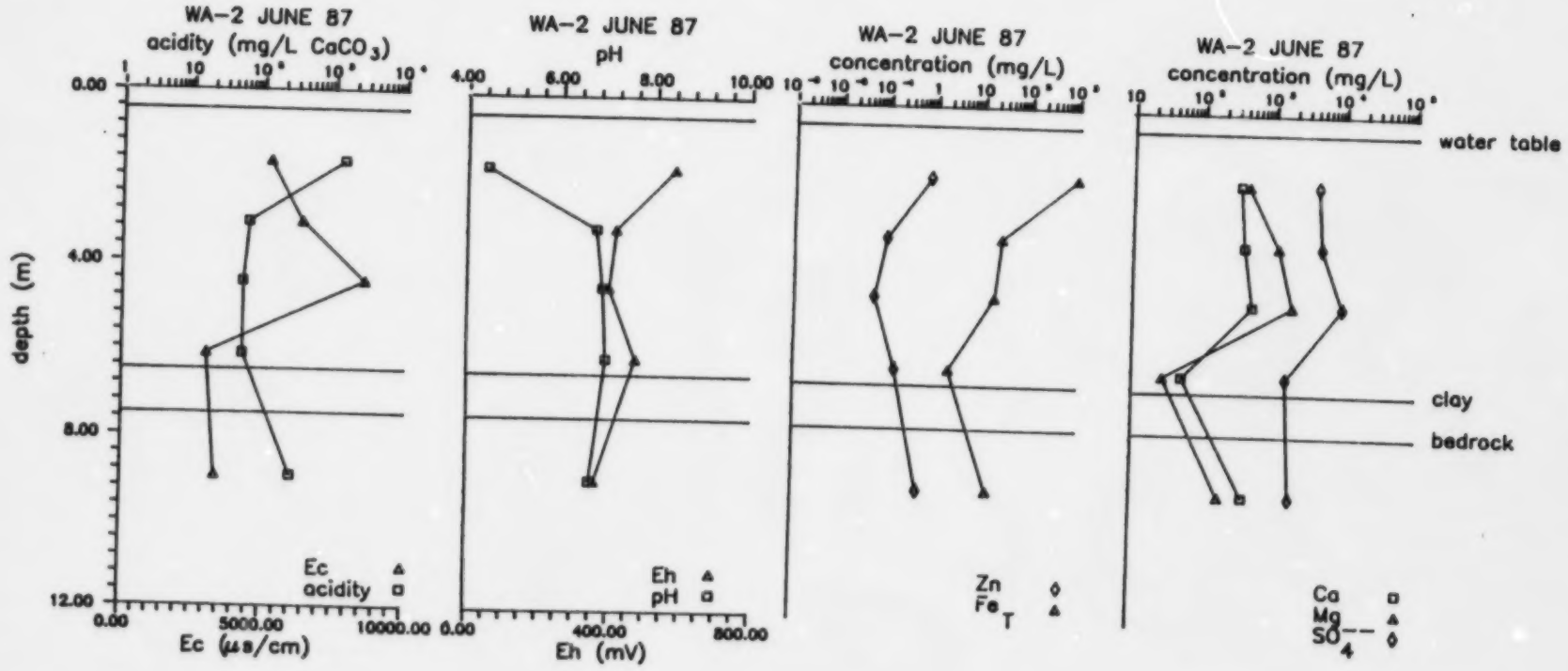


Figure F-1 - June 1987 Chemical/Physical Profiles, Station WA-2

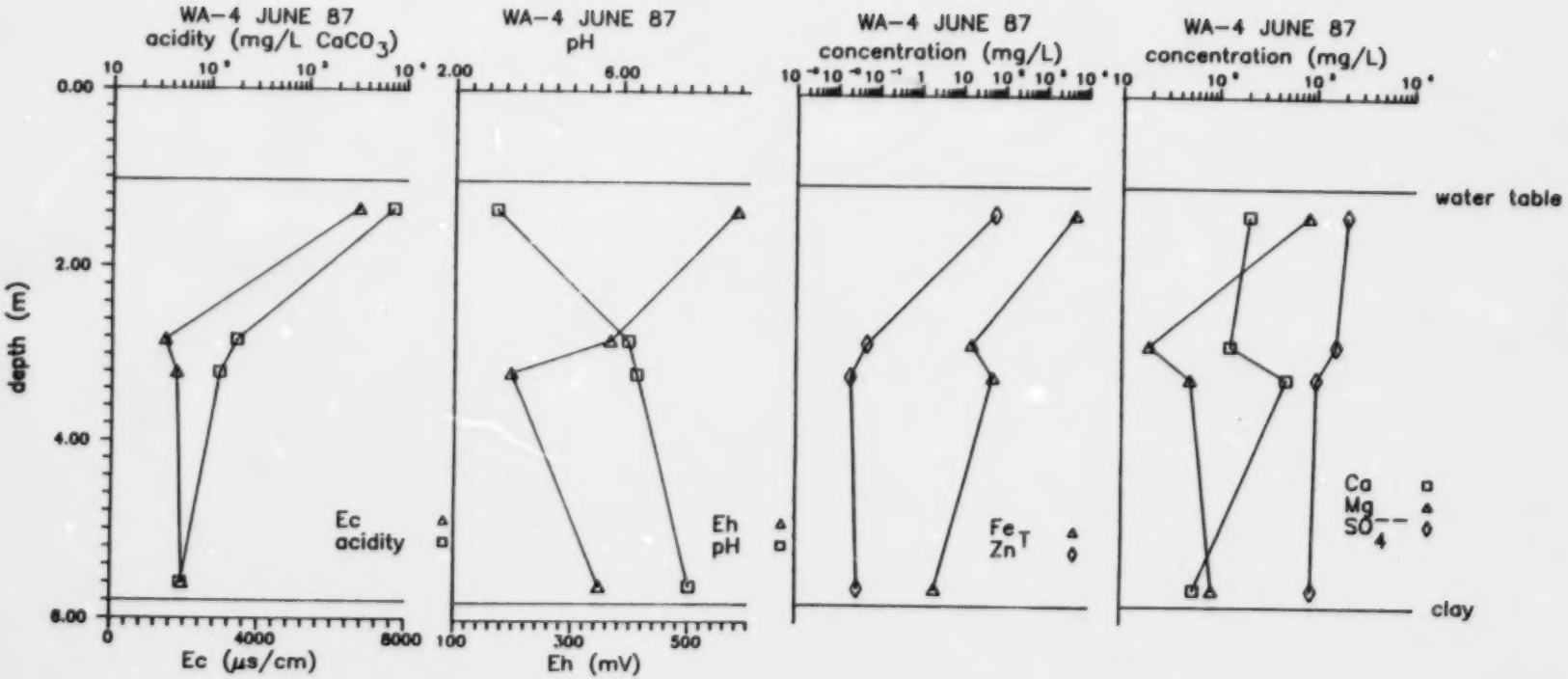


Figure F-2 - June 1987 Chemical/Physical Profiles, Station WA-4

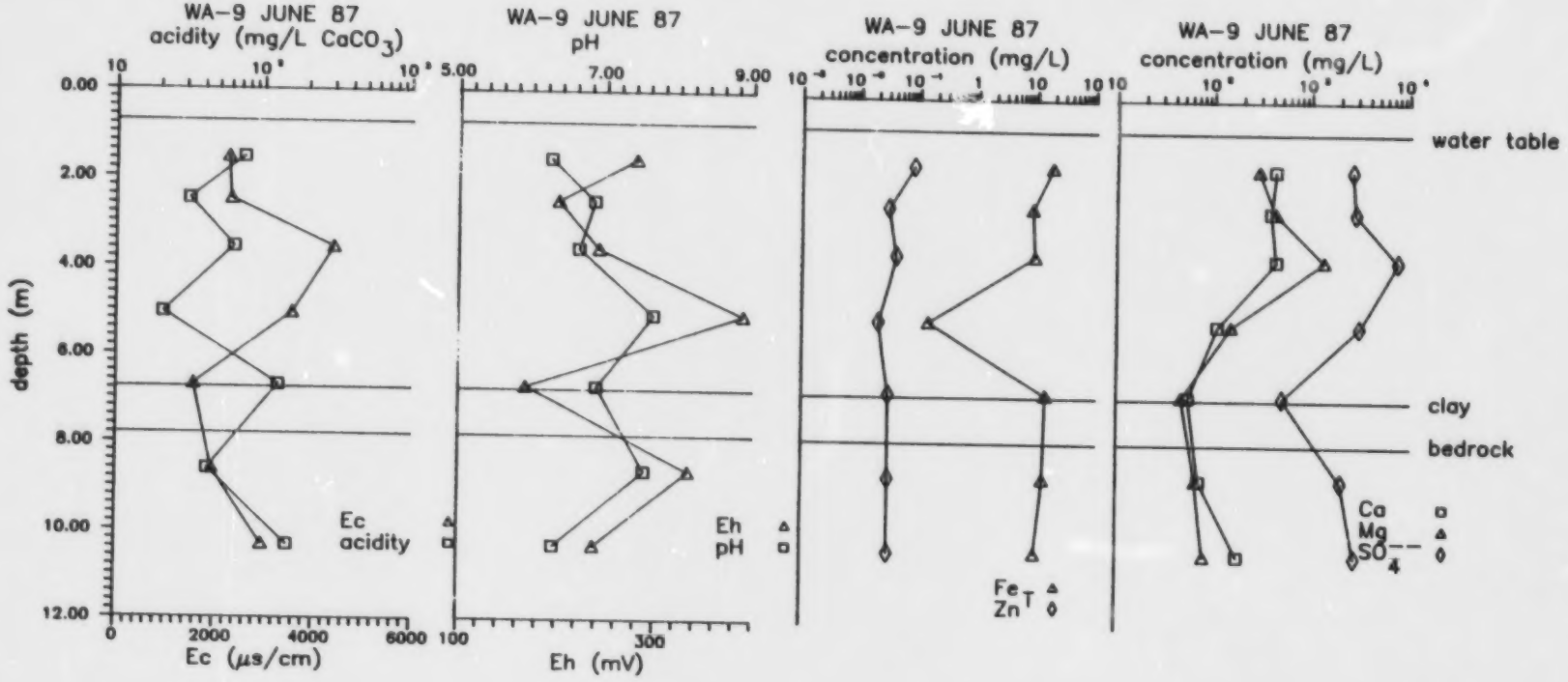


Figure F-3 - June 1987 Chemical/Physical Profiles, Station WA-9

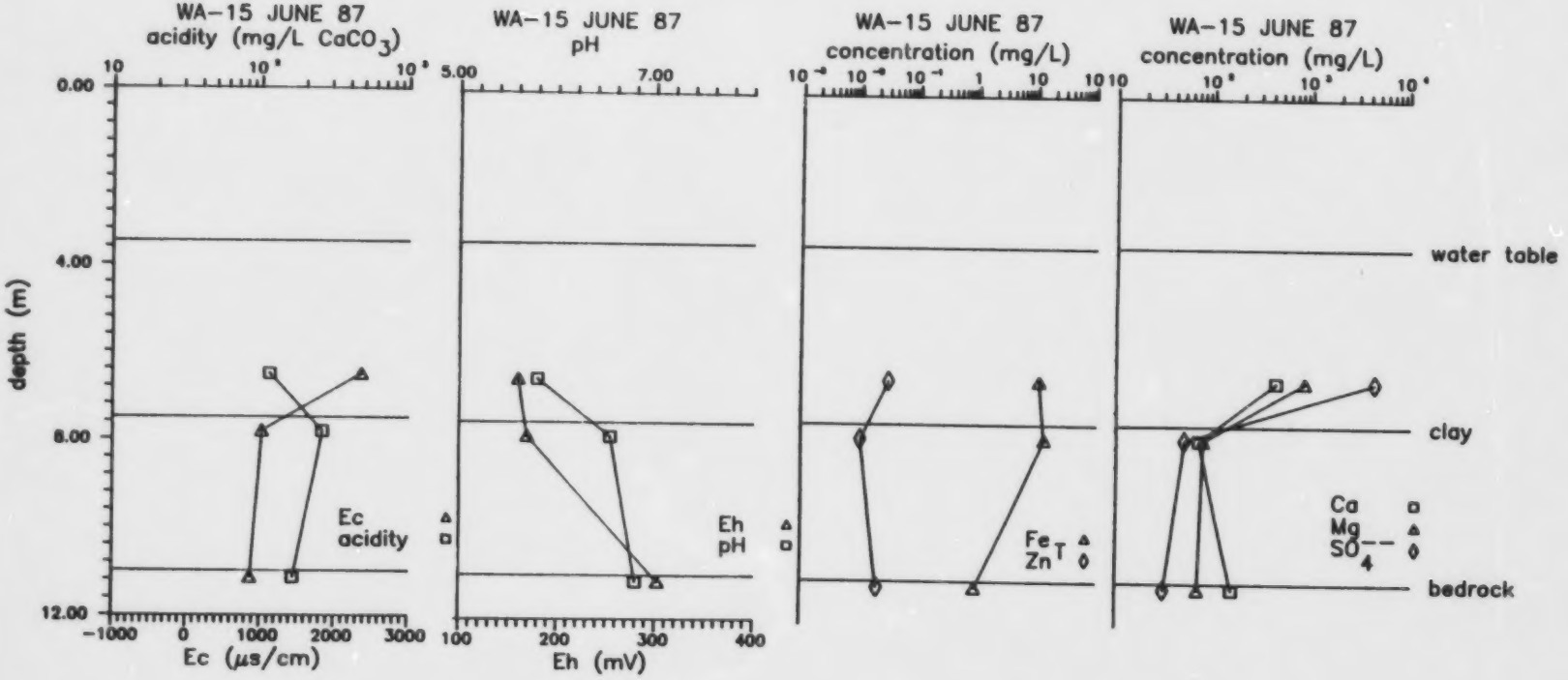


Figure F-4 - June 1987 Chemical/Physical Profiles, Station WA-15

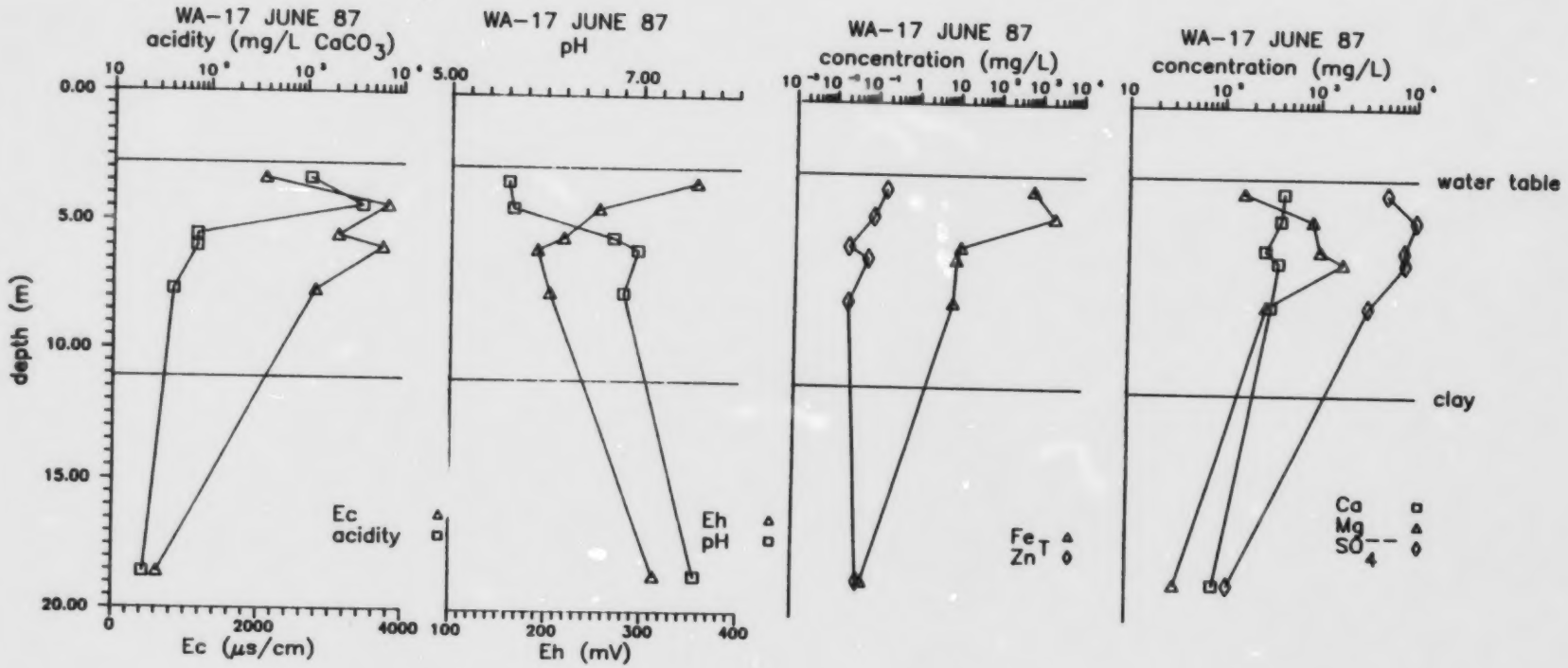


Figure F-5 - June 1987 Chemical/Physical Profiles, Station WA-17

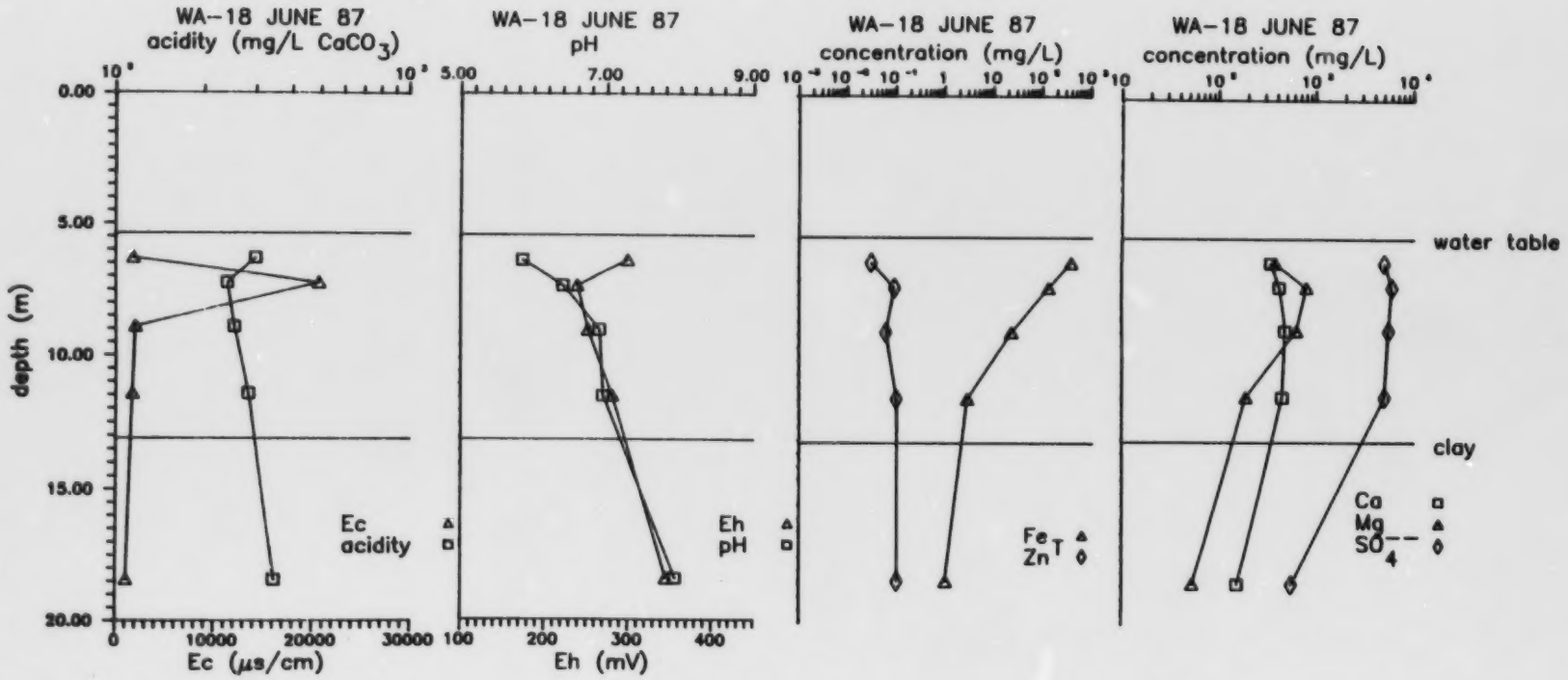


Figure F-6 - June 1987 Chemical/Physical Profiles, Station WA-18

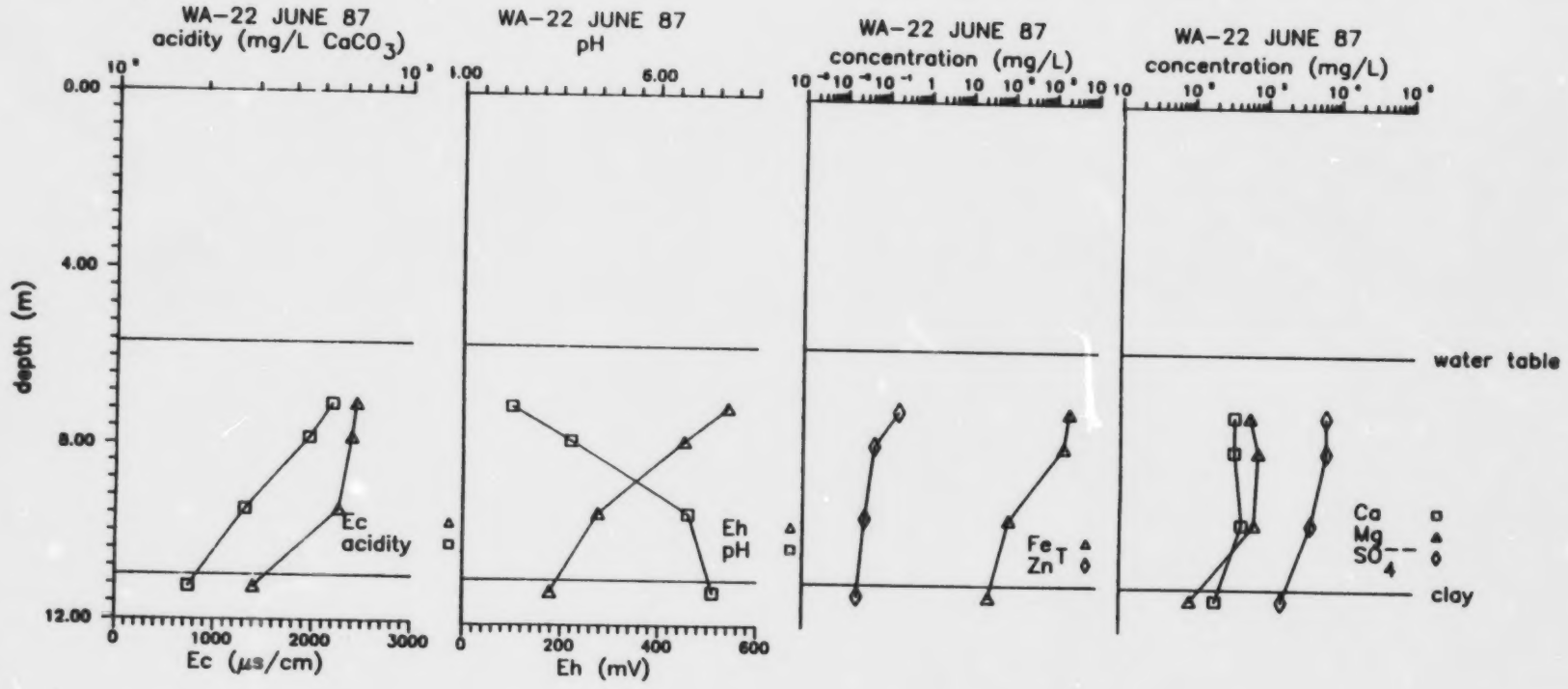


Figure F-7 - June 1987 Chemical/Physical Profiles, Station WA-22

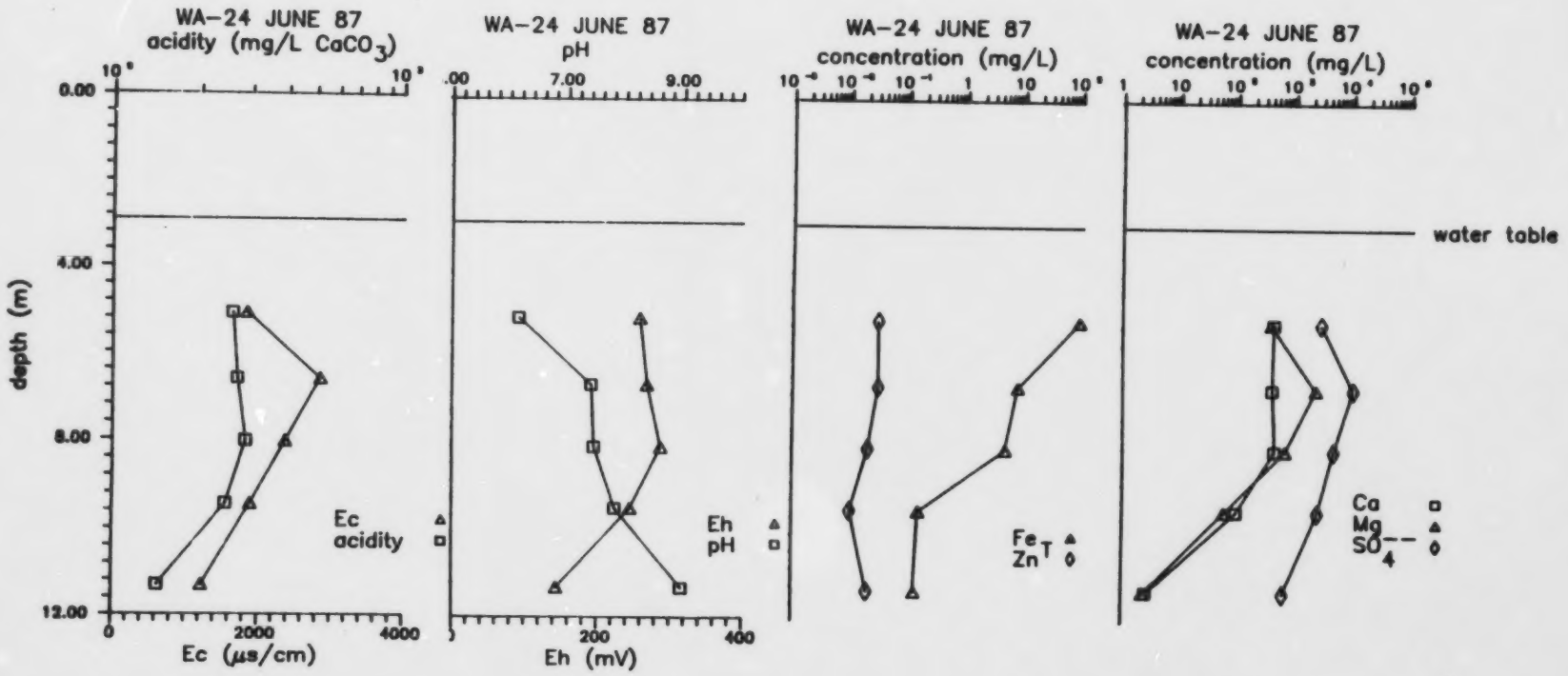


Figure F-8 - June 1987 Chemical/Physical Profiles, Station WA-24

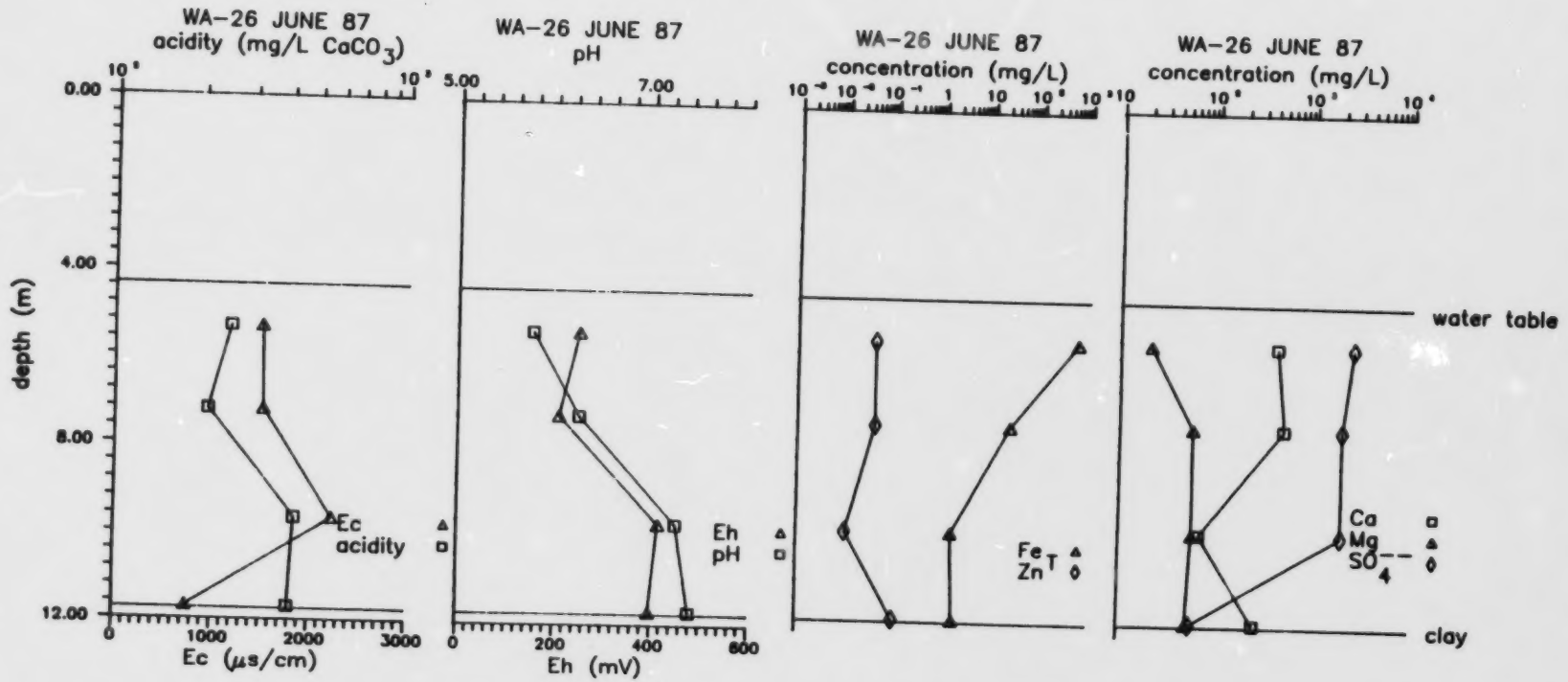


Figure F-9 - June 1987 Chemical/Physical Profiles, Station WA-26

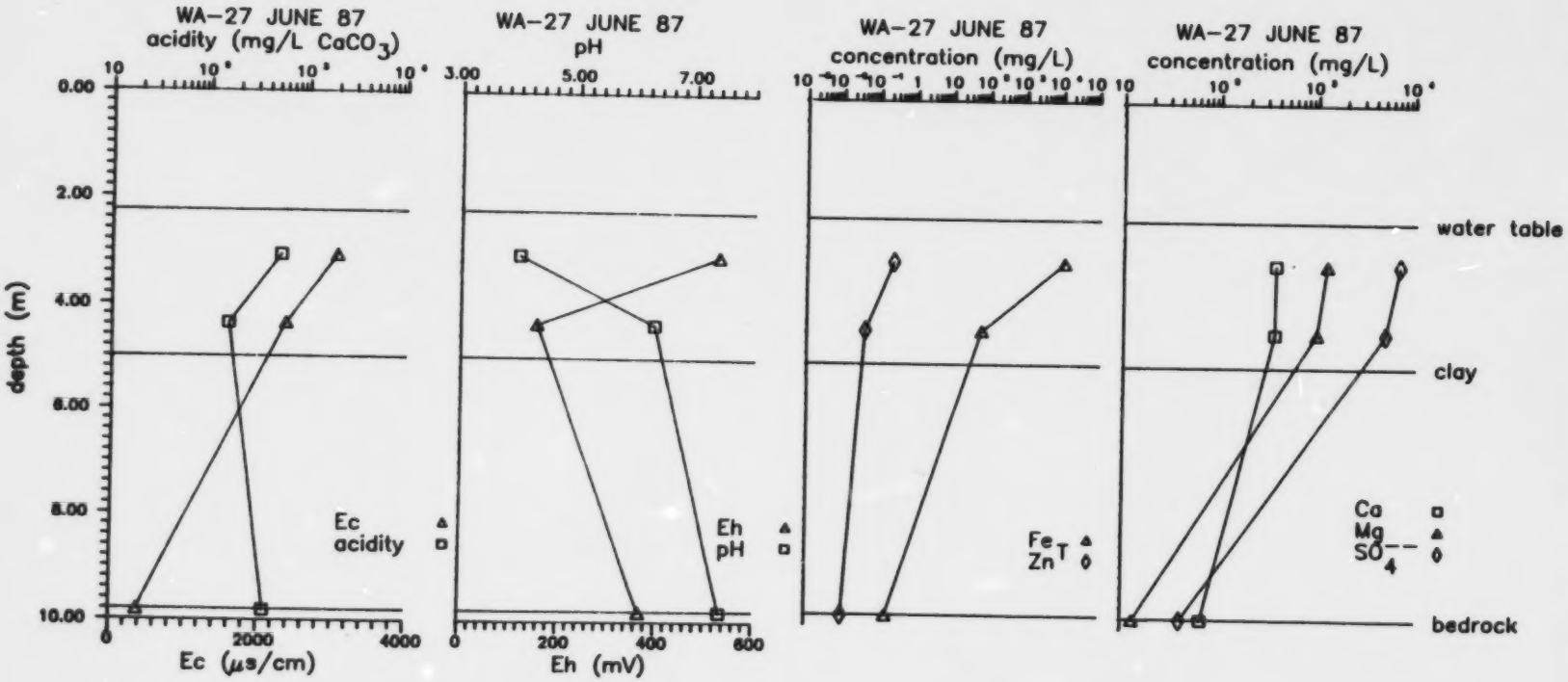


Figure F-10 - June 1987 Chemical/Physical Profiles, Station WA-27

APPENDIX G

SEPTEMBER 1987 SAMPLING PROGRAM - PROFILES OF CHEMICAL/PHYSICAL CHARACTERISTICS OF PORE WATER (Ec, Eh, pH, acidity, Fe_T, Zn, Cu, Mg, SO_4)

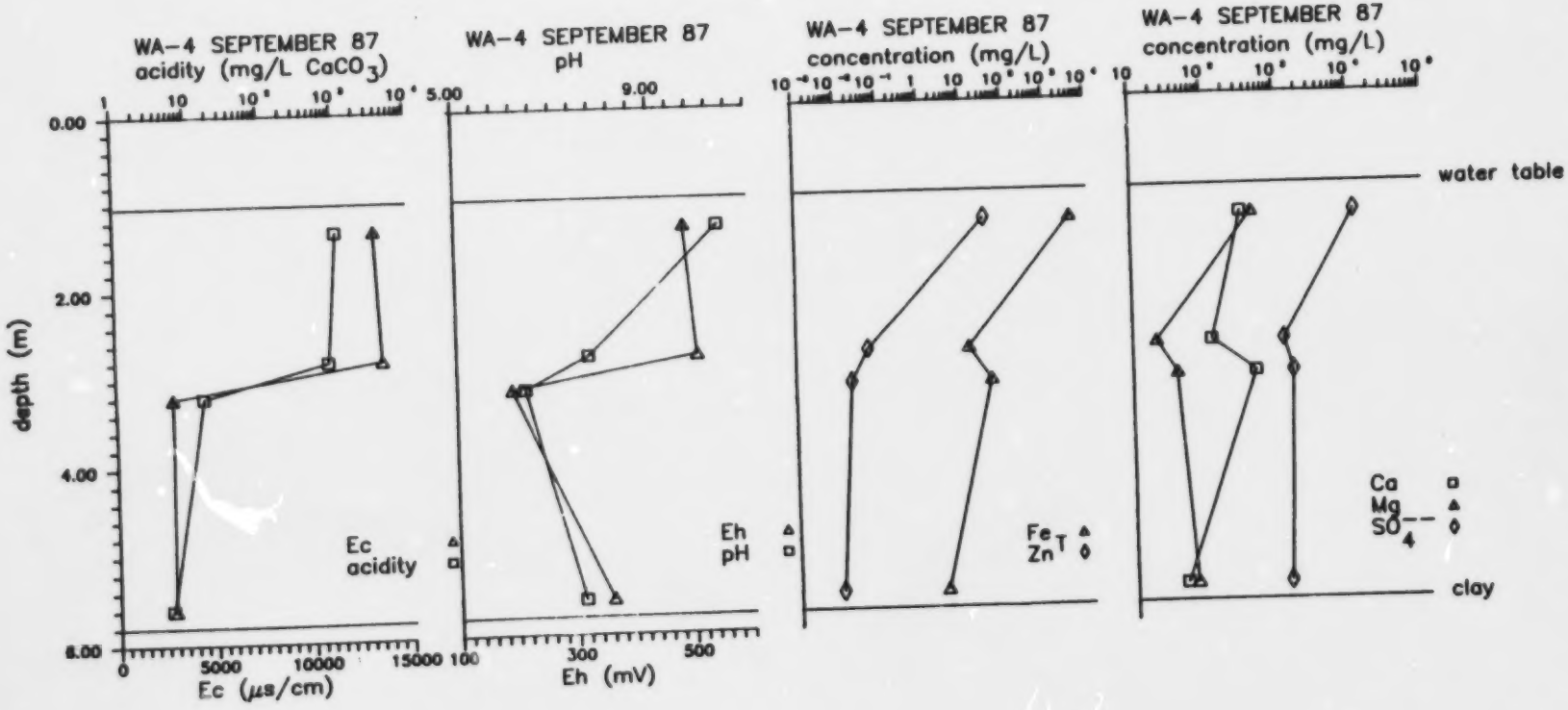


Figure G-1 - September 1987 Chemical/Physical Profiles, Station WA-4

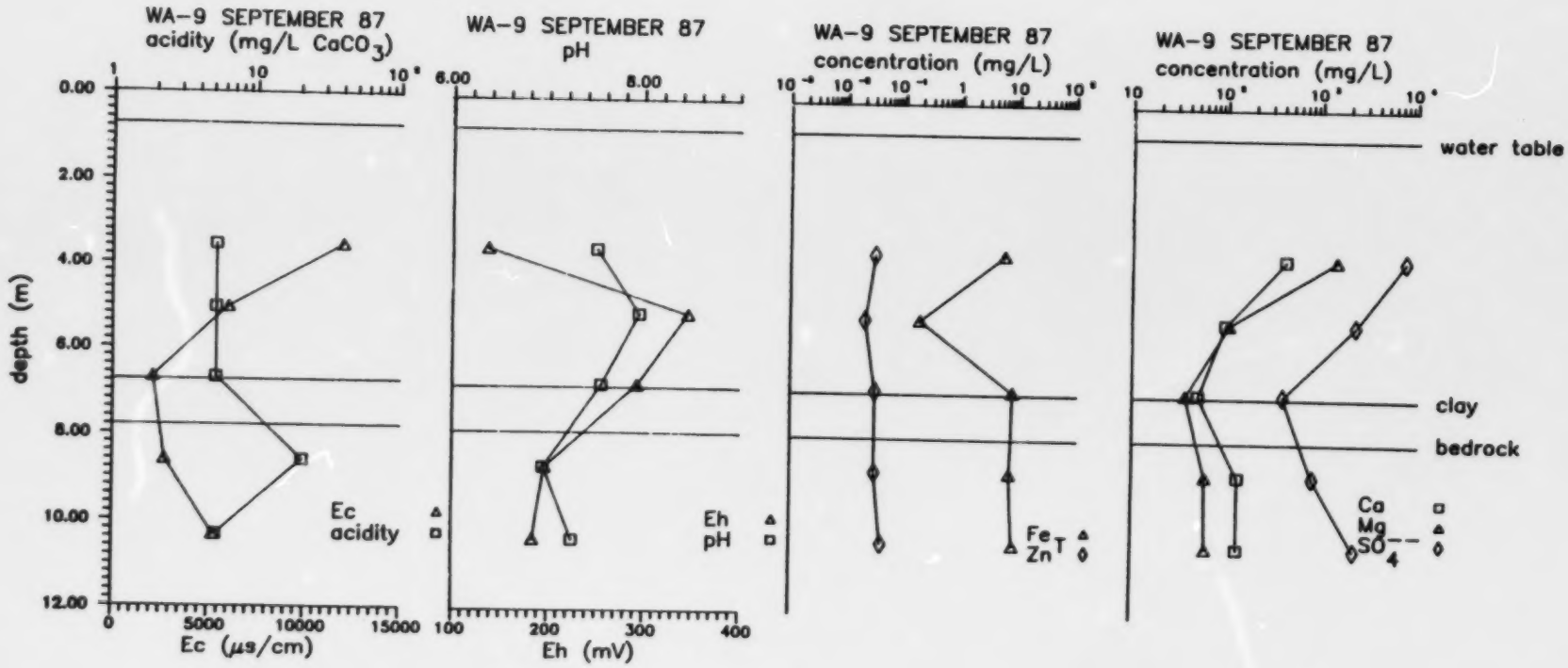


Figure G-2 - September 1987 Chemical/Physical Profiles, Station WA-9

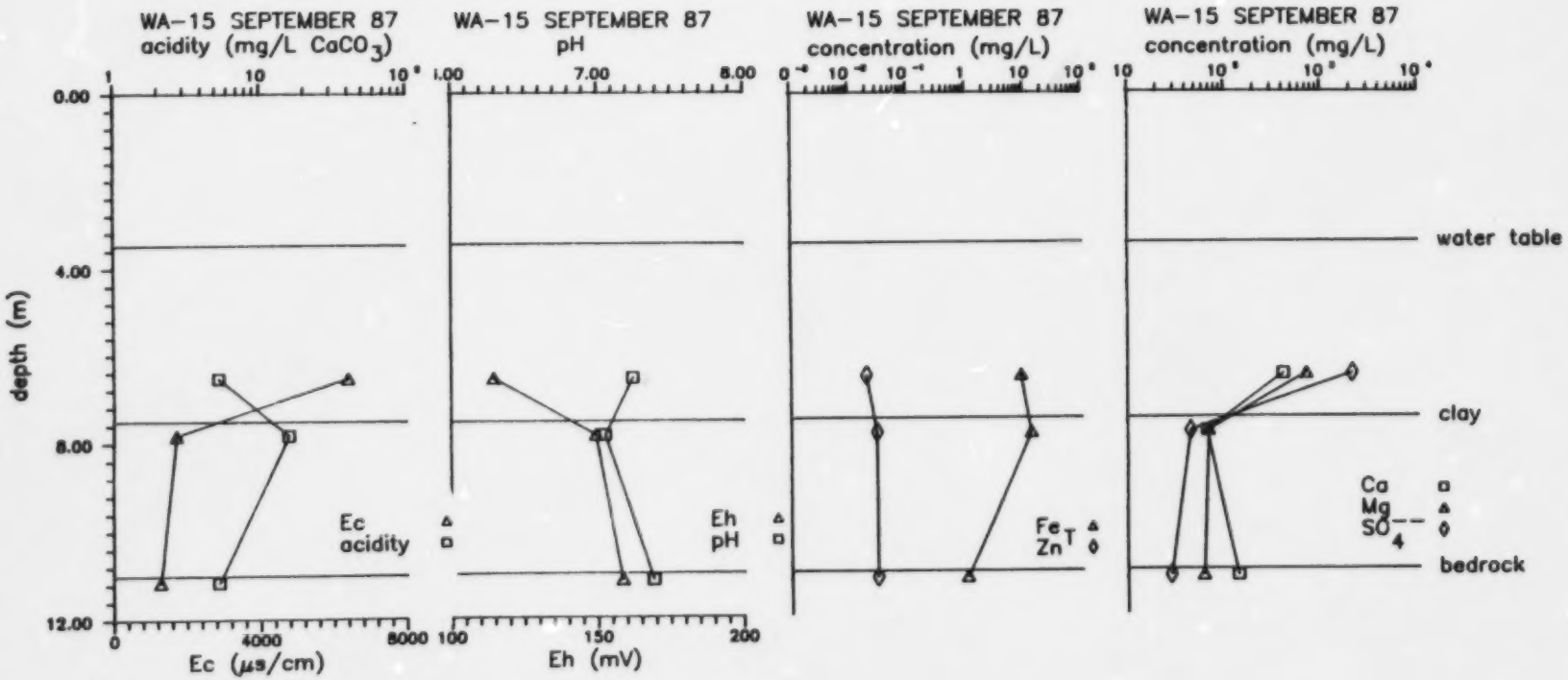


Figure G-3 - September 1987 Chemical/Physical Profiles, Station WA-15

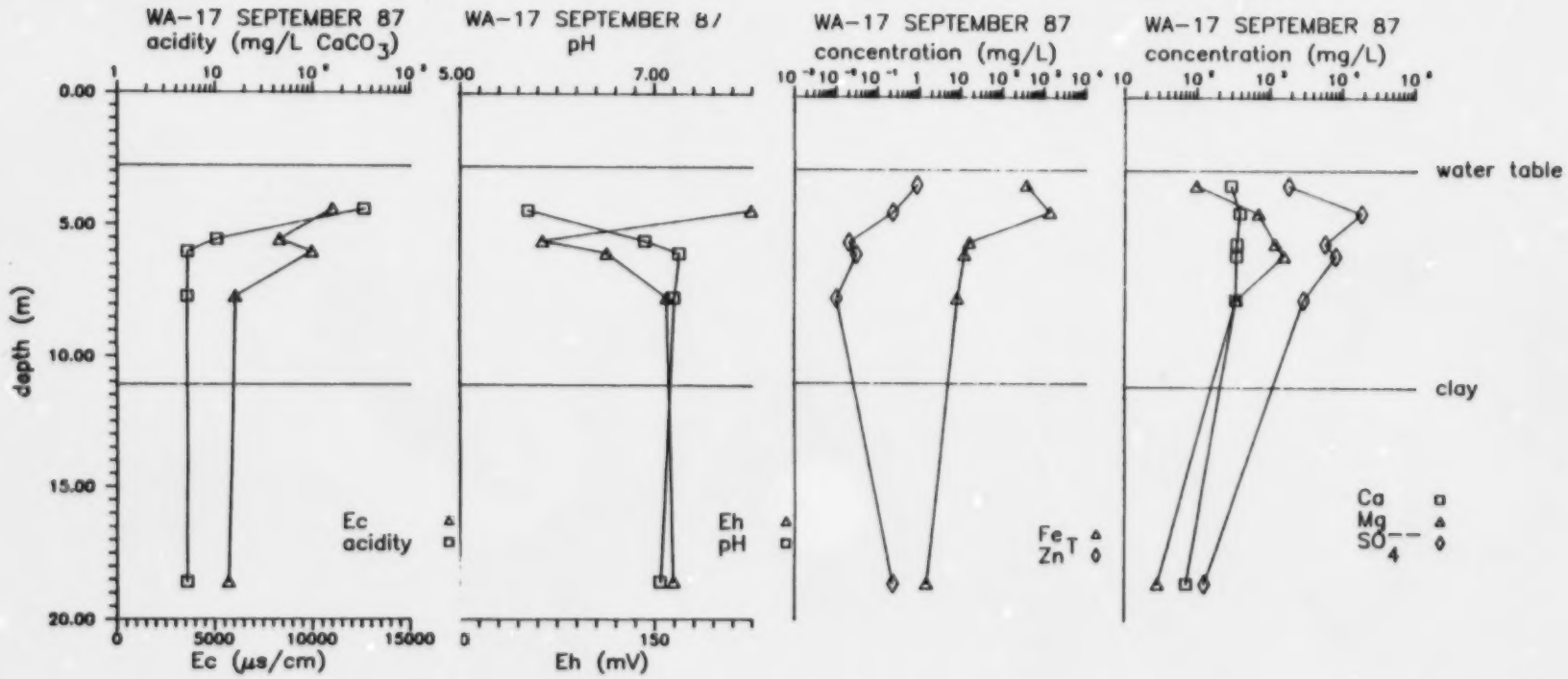


Figure G-4 - September 1987 Chemical/Physical Profiles, Station WA-17

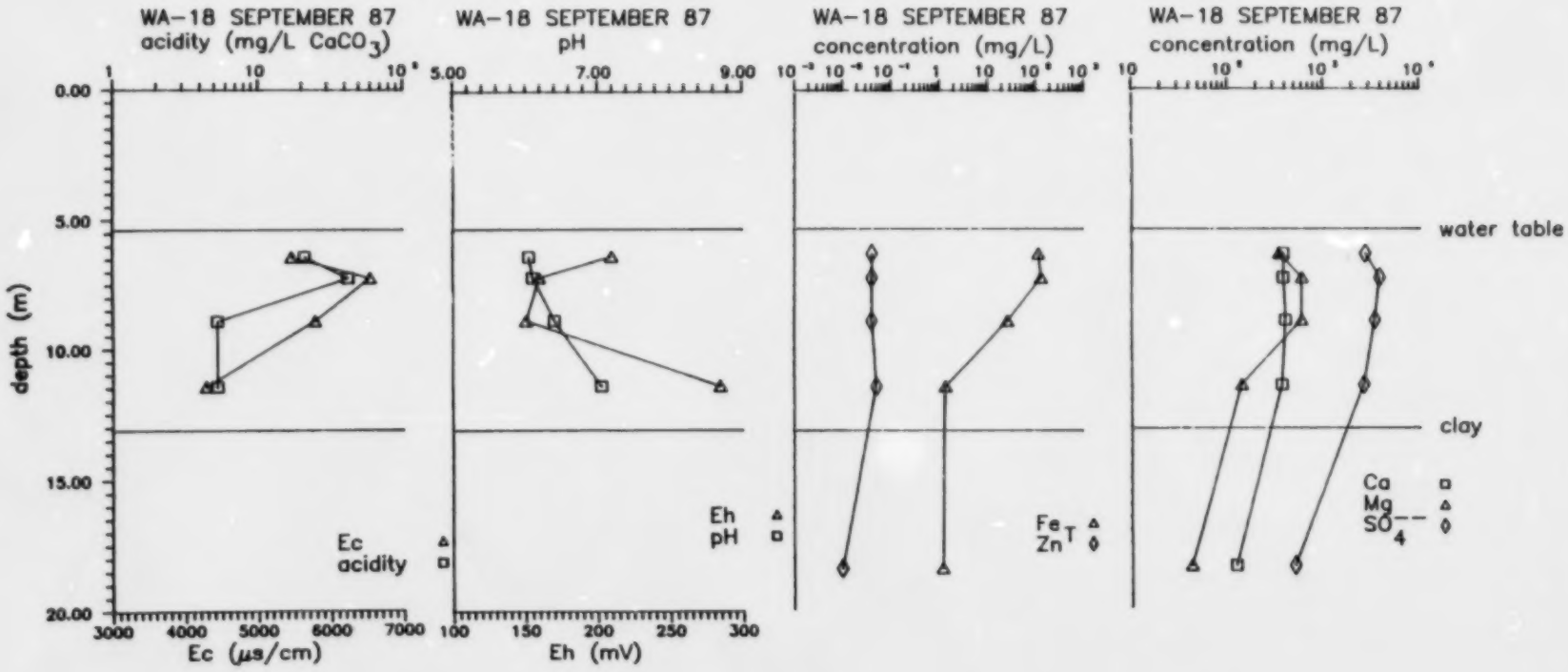


Figure G-5 - September 1987 Chemical/Physical Profiles, Station WA-18

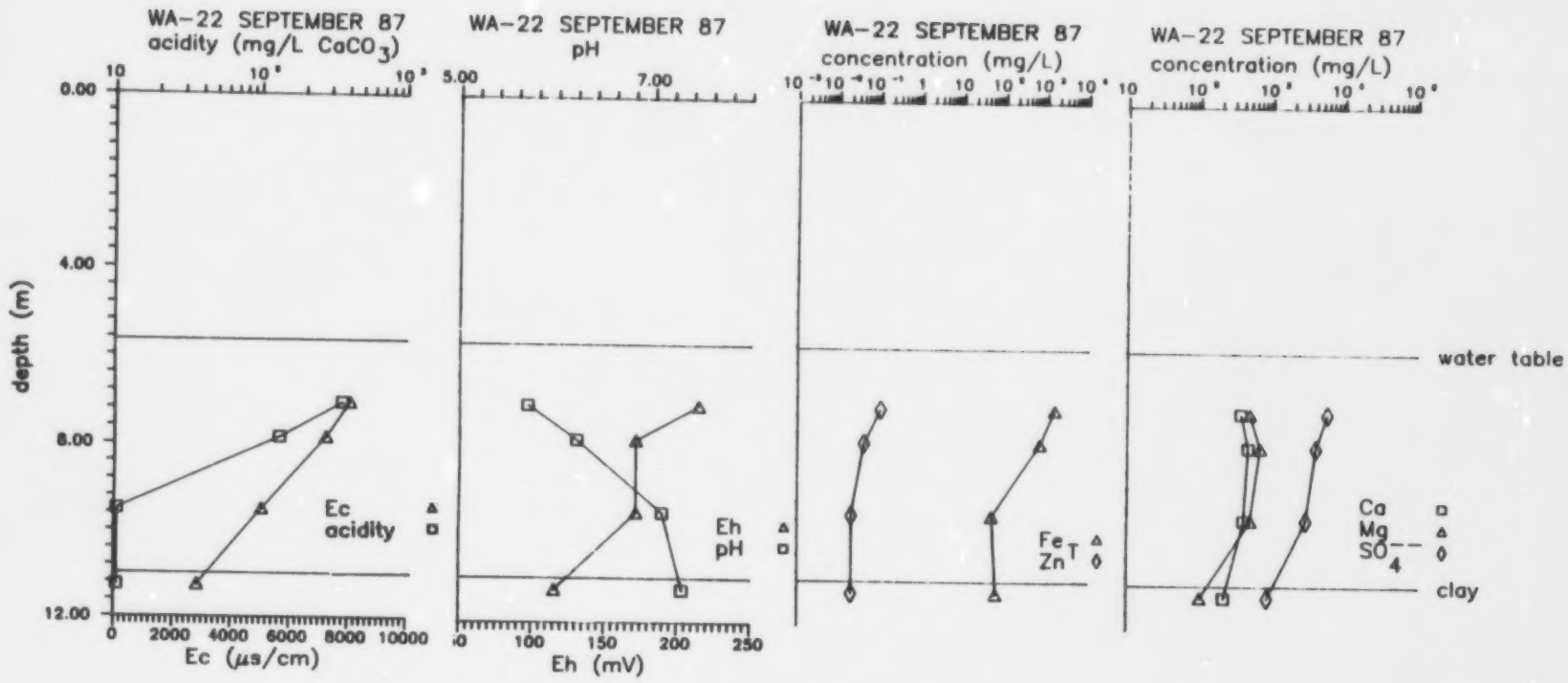


Figure G-6 - September 1987 Chemical/Physical Profiles, Station WA-22

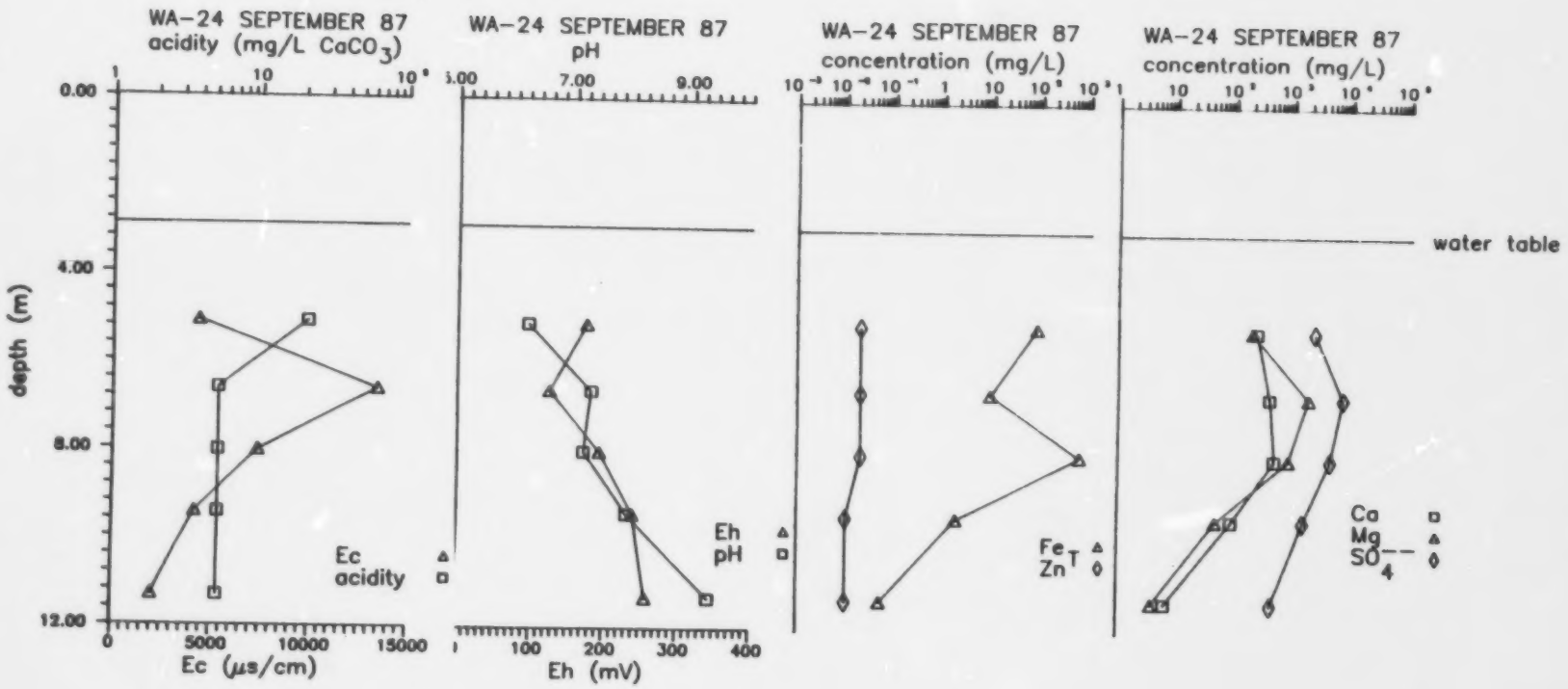


Figure G-7 - September 1987 Chemical/Physical Profiles, Station WA-24

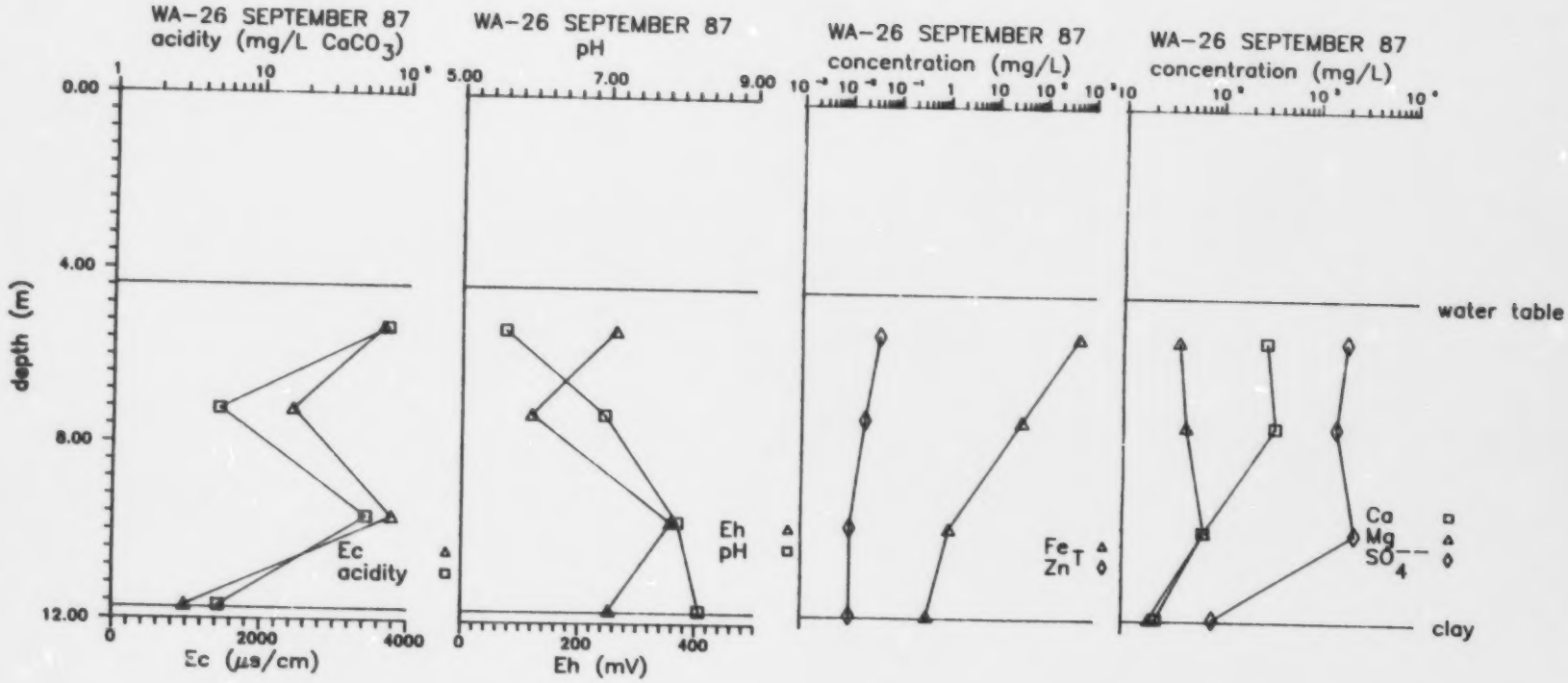


Figure G-8 - September 1987 Chemical/Physical Profiles, Station WA-26

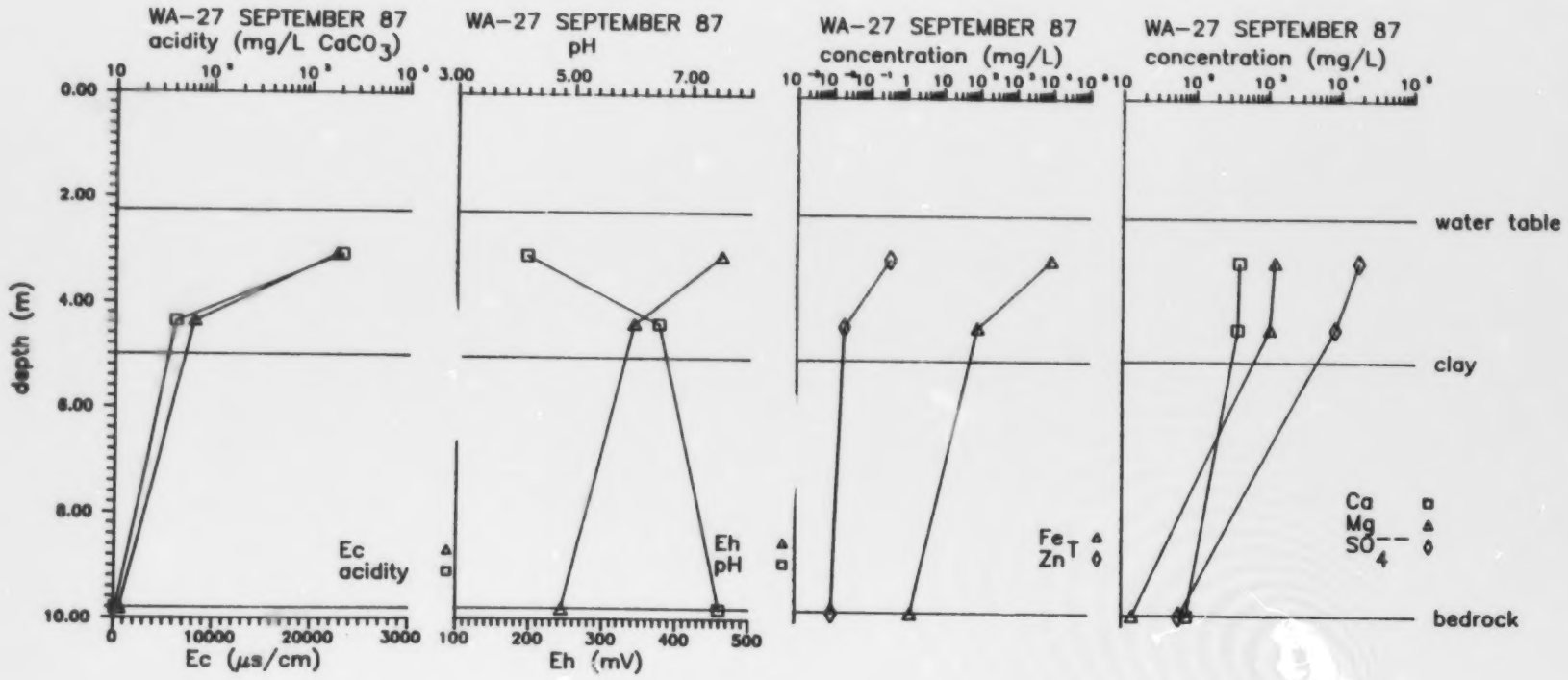


Figure G-9 - September 1987 Chemical/Physical Profiles, Station WA-27

APPENDIX H

COMPARISON OF CHEMICAL CHARACTERISTICS OF PORE WATER (Fe_T, Ca, Mg, SO_4) FOR THREE SAMPLING ROUNDS:

- October 1986
- June 1987
- September 1987

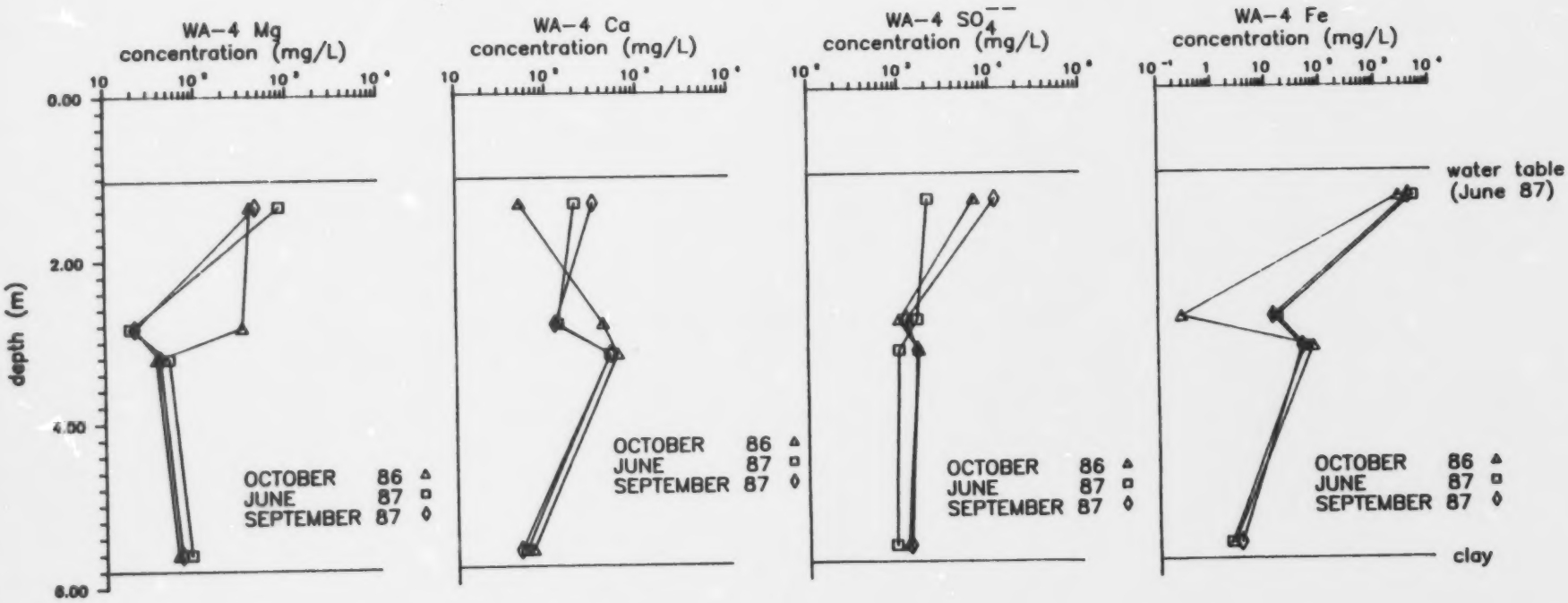


Figure H-1 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-4

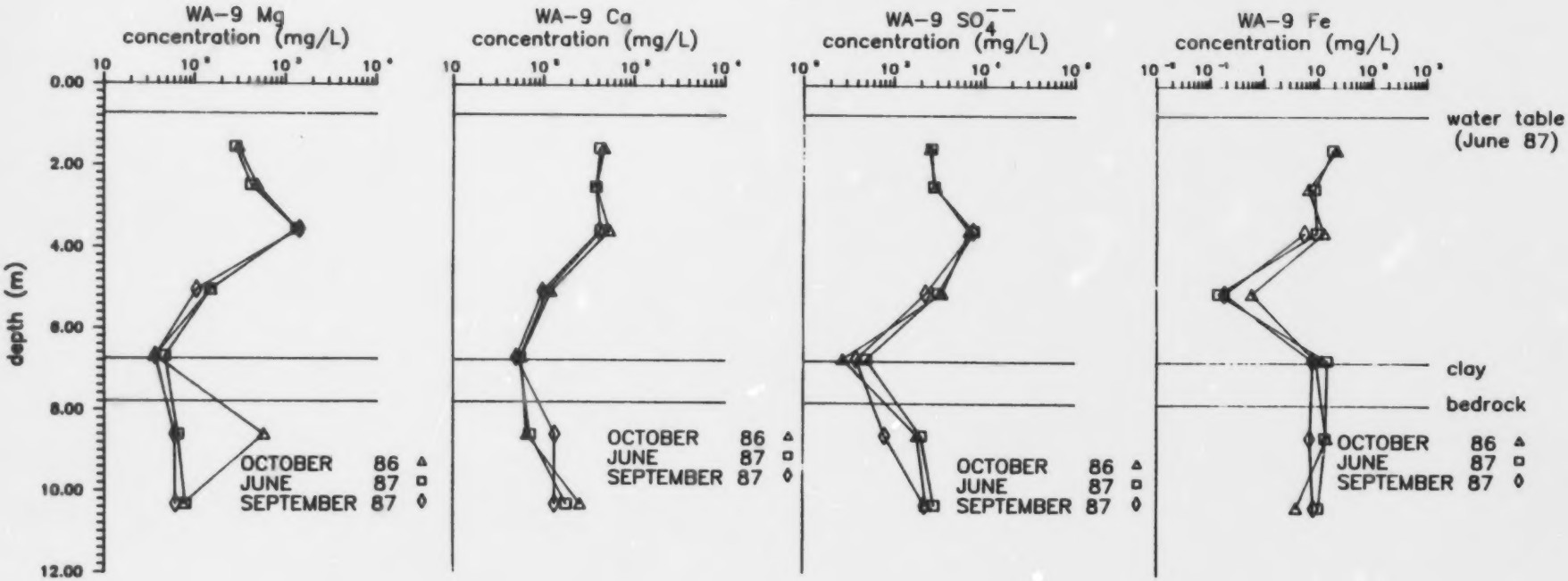


Figure H-2 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-9

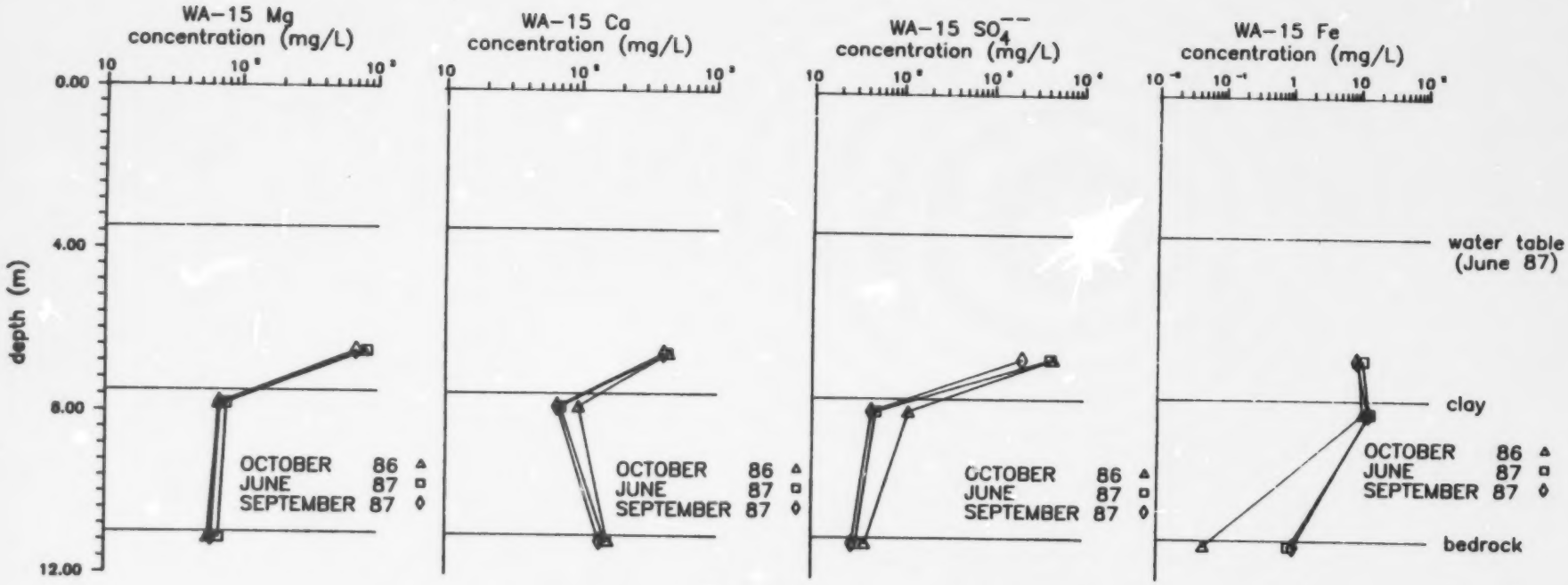


Figure H-3 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-15

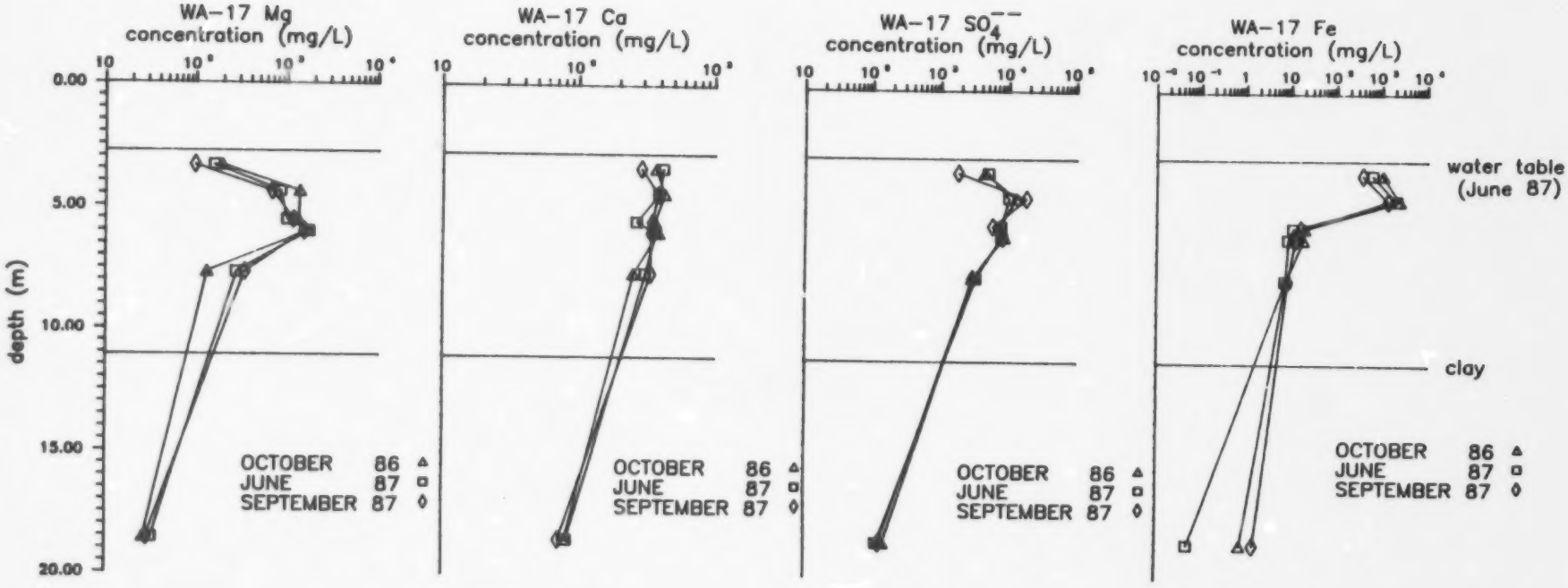


Figure H-4 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-17

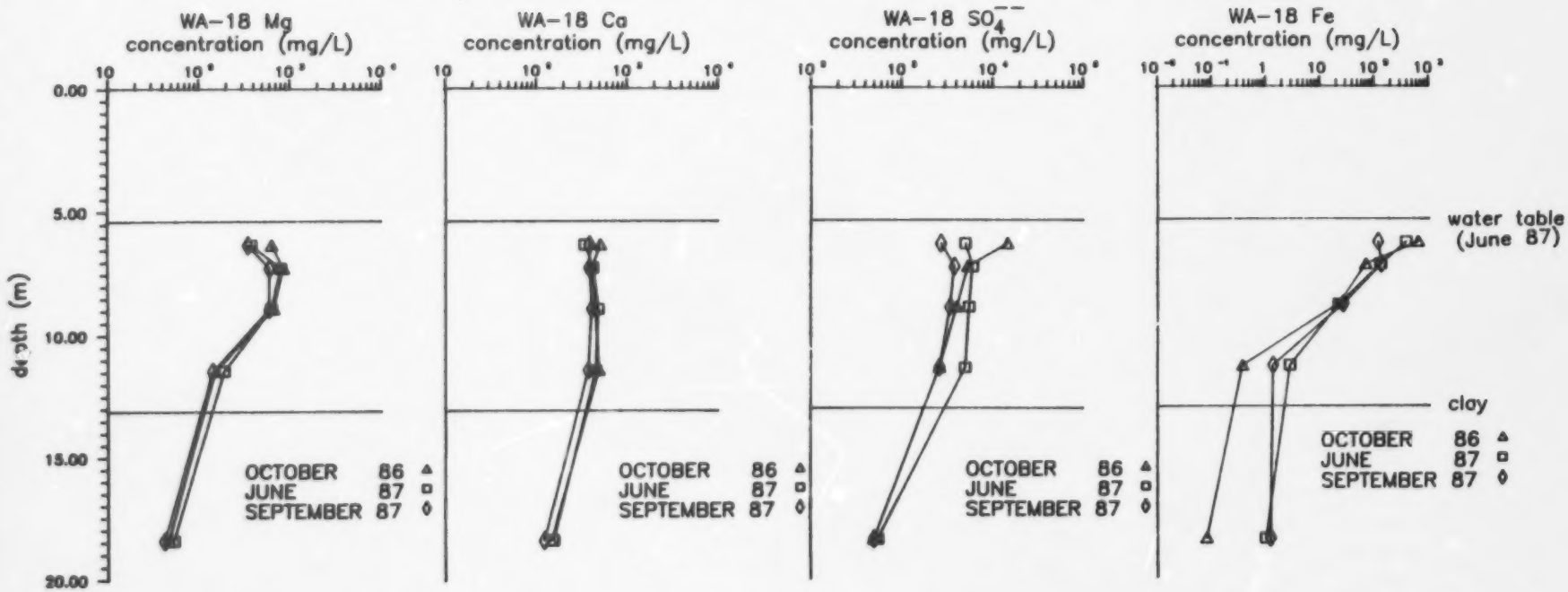


Figure H-5 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-18

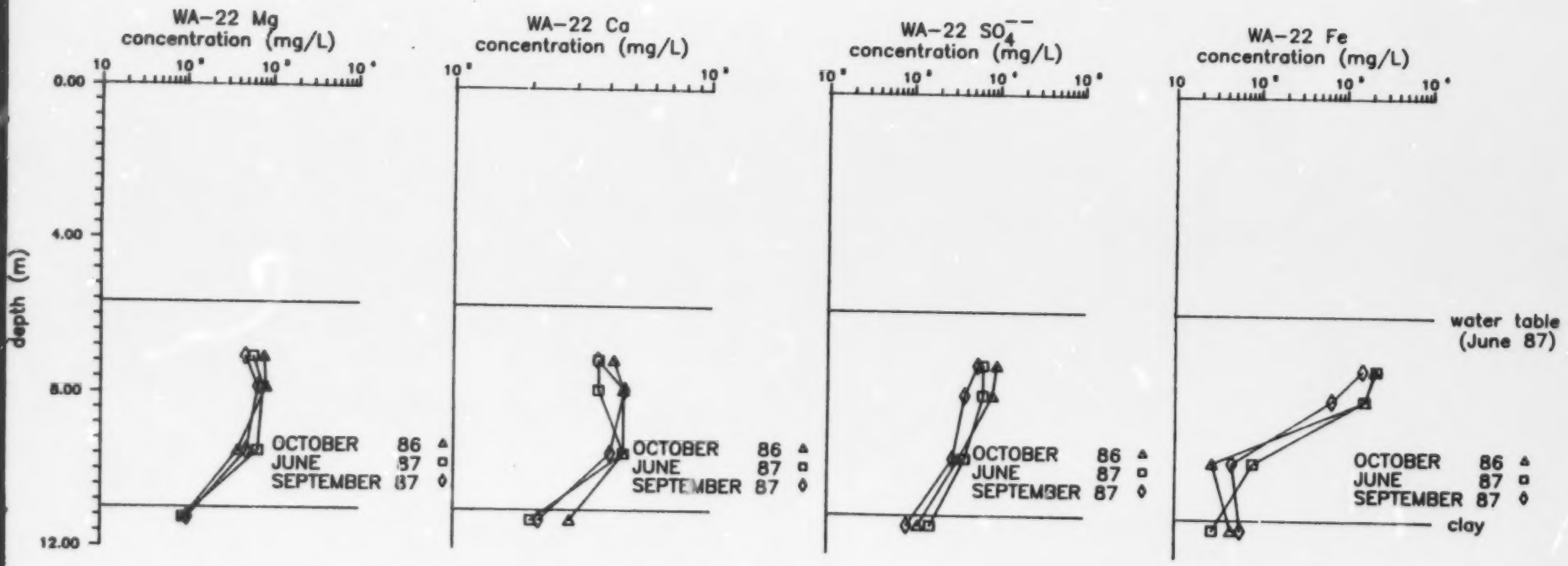


Figure H-6 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-22

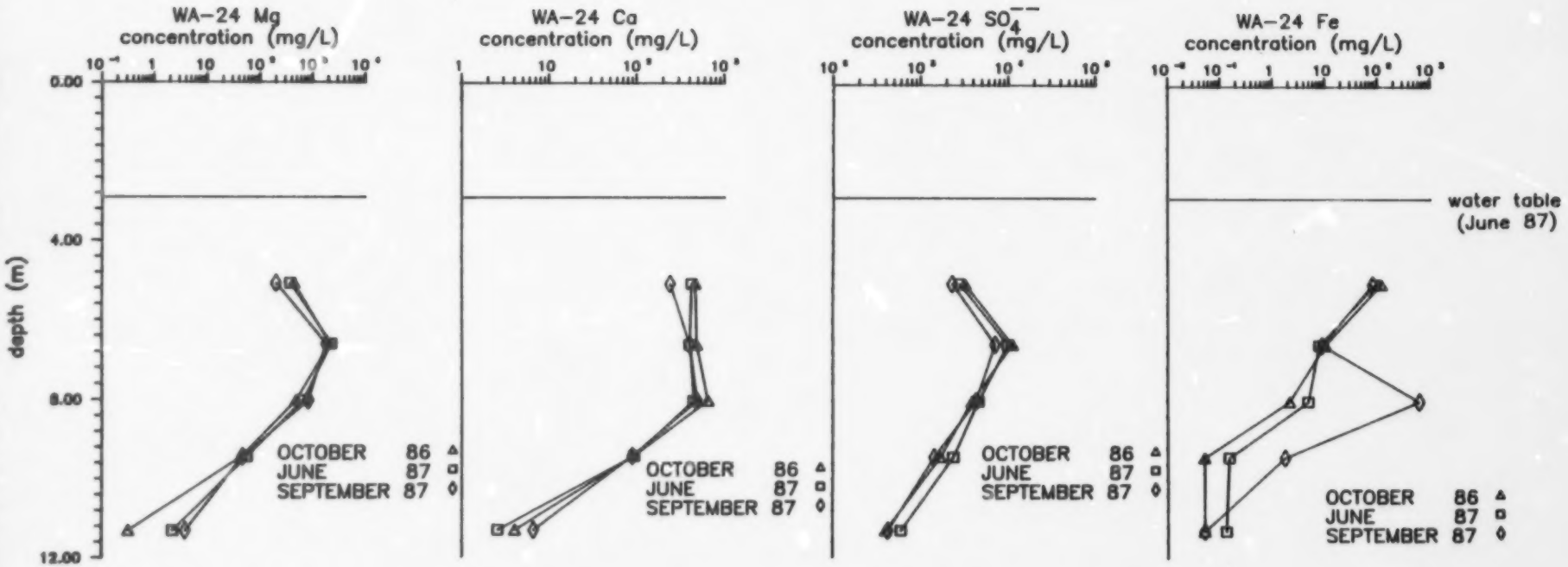


Figure H-7 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-24

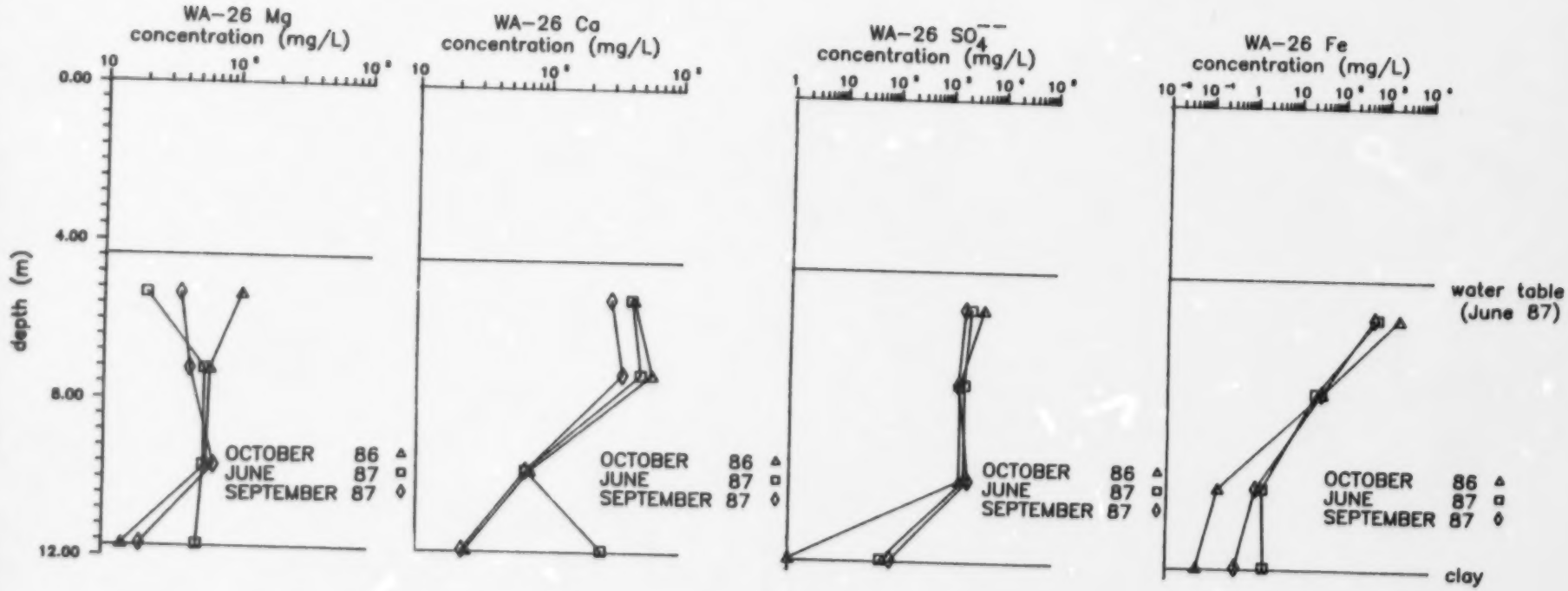


Figure H-8 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-26

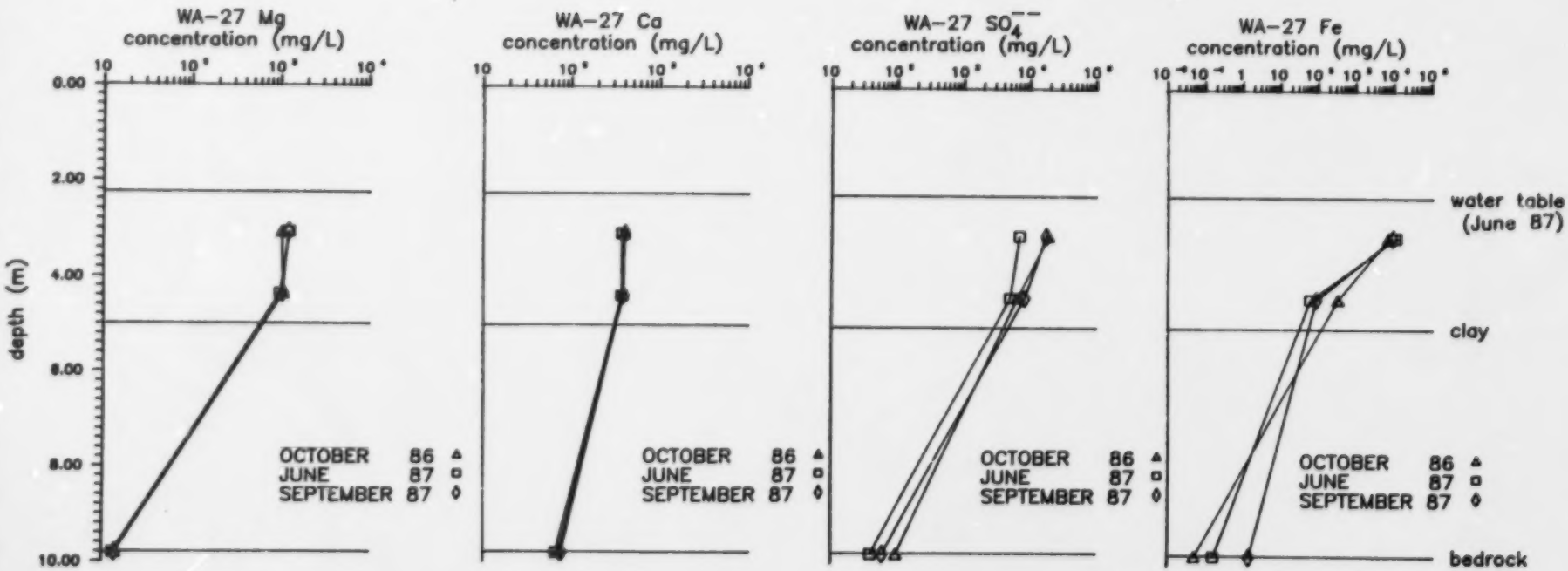


Figure H-9 - Chemical Profiles, October 1986, June 1987, September 1987, Station WA-27

Volume

3

PORE WATER GEOCHEMISTRY AND MINERALOGY OF VADOSE ZONE OF SULPHIDE TAILINGS, WAITE AMULET, QUEBEC

AS PART OF

THE HYDROGEOCHEMICAL INVESTIGATION OF REACTIVE TAILINGS AT WAITE AMULET TAILINGS SITE, NORANDA, QUEBEC

PHASE 3 - 1987 PROGRAM

SUPPLEMENTARY REPORT

DSS File Number :	03SQ.23440-7-9161
DSS Contract Serial Number :	23440-7-9161/01-SQ
CANMET Scientific Authority :	Dr. N.K. Dave
Project Manager :	R.S. Siwik
Authors :	D. Blowes and J. Jambor

84 pp

MICROMEDIA

SUMMARY

The Mine Environment Neutral Drainage (MEND) Program is jointly funded by CANMET, the provinces and the mining industry. It has the objective of developing an inventory of practical techniques to achieve sufficient reduction in the impact of acid-generating tailings and wasterock to permit ultimate abandonment without ongoing treatment or maintenance.

The Waite Amulet project within this program is a multi-year study with the overall objective of developing a better understanding of the hydrogeochemical processes and changes which occur in an acid-generating tailings area, as the basis for identifying and developing improved tailings management methods. Phase 1 (1985) included a preliminary site reconnaissance and drilling program. Phase 2 (1986) completed the definition of the site hydrogeology, evaluated the geochemistry of the unsaturated zone, and identified oxidation control options for 1987 field evaluation; equipment for monitoring precipitation, surface water and seepage was also purchased.

The 1987 field work (Phase 3) had four objectives: i) install the facilities required to develop water budgets and metal loadings; ii) relate mineralogy to the vadose zone pore water chemistry; iii) evaluate oxygen diffusion into the tailings; iv) monitor pore water movement and site geochemistry.

The water monitoring facilities were installed, checked out and a limited amount of data collected. Oxygen profiles were established in sections of the tailings that were vegetated, bare and clay covered. Hydraulic conductivities have been established, the water table was monitored and extensive pore water analyses obtained. The work was documented in the report to DSS by Siwik, St. Arnaud, Prairie and Labrosse, in May 1988.

This supplementary report details an evaluation of mineralogical changes by J. Jambor of CANMET and the related assessment of vadose zone water chemistry by D. Blowes of University of Waterloo.

The Pore-Water Geochemistry and the Mineralogy of the Vadose Zone of Sulfide Tailings, Waite Amulet, Quebec

by

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Abstract

Low-pH waters, requiring treatment because of high concentrations of dissolved metals, are being discharged from a decommissioned tailings impoundment at the Waite Amulet Zn-Cu mine site in northeastern Quebec, Canada. A detailed study of the vadose zone of the tailings comparing mineralogical and geochemical analyses of the tailings solids with geochemical analysis of the tailings pore water and pore gas indicates the presence of three zones within the tailings. These zones include an upper sulfide-depleted zone, where the sulfides have been extensively removed and oxidation is largely complete, an intermediate zone, where sulfide oxidation and acid neutralization reactions are occurring, and an unoxidized zone below the depth of oxygen penetration, where sulfides are unoxidized. High concentrations of dissolved solids are being displaced down through the unoxidized zone from the sulfide-depleted zone toward the water table. Sulfide-oxidation and acid neutralization reactions have generated concentrations of dissolved solids high enough to lead to the precipitation of a series of secondary solid phases. Precipitation-dissolution reactions involving these solid phases control the concentrations of the major ions in the tailings pore water. Concentrations of dissolved metals are controlled by precipitation-dissolution, crystal-structural replacement, and adsorption/coprecipitation reactions. Predictions based on the observed data and numerical simulations suggest that, in the absence of an effective remedial program, sulfide oxidation and H^+ production will continue for several centuries.

INTRODUCTION

The Waite Amulet mill, in northeastern Quebec (Fig. 1), processed approximately 8.74 million tonnes of sulfide ore between opening in 1929 and final mill closure in 1962. The predominantly Zn-Cu massive-sulfide-type ore was derived from 10 separate ore bodies in the vicinity of the mill. The mill produced Cu and Zn concentrates and later additional pyrite concentrates. In addition, the mill generated approximately 5.9 million tonnes of mill tailings, which are contained in an elevated 41-ha tailings dam adjacent to the site. These tailings are rich in sulfide minerals, principally pyrite and pyrrhotite, which oxidize readily when exposed to water and atmospheric oxygen. The oxidation of sulfide minerals has generated low-pH conditions and high concentrations of SO_4^{2-}, Fe^{2+}, and other metals. The movement of tailings-derived water away from the impoundment and into adjoining surface and groundwater flow systems constitutes an important environmental problem.

Oxidation of sulfide minerals at the Waite Amulet site and the accompanying degradation in surface water quality was recognized in the late 1960's, and steps were taken to reduce the environmental impact of the tailings. These steps included the construction and maintenance of a water treatment plant and the successful completion of a tailings revegetation program. In the early 1980's it was realized that the completion of the revegetation program would not stop the oxidation of sulfide minerals in the tailings impoundment (VELDHUIZEN et al., 1987).

In 1985 an extensive research program was undertaken at the Waite Amulet site to improve the understanding of the geochemical evolution of sulfide tailings and to develop more effective predictive and remedial techniques for the environmental problems associated with sulfide tailings. The Waite Amulet tailings impoundment was selected for this research because these tailings were extensively studied during the development of the tailings revegetation program, are accessible and in the vicinity of laboratory facilities, and because a variety of hydrogeologic conditions are present at this site. This research program included investigation of the hydrology, hydrogeology, mineralogy and geochemistry of the inactive tailings impoundment (DAVE et al., 1986; SIWIK, 1986; SIWIK et al., 1987; PETRUK and PINARD, 1986; and JAMBOR, 1987a, 1987b).

The geochemistry and mineralogy of the vadose zone of the Waite Amulet tailings are described in this paper.

The vadose zone is the zone of partial water saturation, above the water table, where gaseous atmospheric oxygen can diffuse into the tailings and where sulfide oxidation reactions occur. Geochemical analysis of the tailings pore water provides information concerning the distribution and concentrations of dissolved constituents within the tailings, and provides an indication of the direction and rate of tailings pore-water movement. Pore-water and pore-gas chemistry data, when combined with geochemical-speciation mass-transfer modelling, provide an indication of the geochemical equilibrium reactions controlling the concentrations of dissolved constituents. Analysis of the tailings solids indicates the extent of sulfide weathering, the nature of the major secondary precipitates, and the

nature and extent of non-equilibrium reactions such as silicate dissolution and replacement reactions. One of the principal values of mineralogical analysis is that it definitively determines the presence both of the primary and the secondary minerals, the presences of which are only inferred in the geochemical modelling. A corresponding benefit of pore-water and pore-gas analysis is that the geochemical equilibrium reactions controlling the concentrations of many minor constituents can be inferred, because the detection limits of dissolved constituents are frequently low relative to equilibrium solubility concentrations. This is particularly valuable in instances where the quantities of secondary precipitates are too small to isolate by standard techniques of mineralogical analysis. Consequently, a detailed mineralogical analysis of the tailings solids conducted in conjunction with detailed tailings pore-water and pore-gas analysis provides greater insight into the future geochemical evolution of the tailings than either of the two approaches could independently.

PREVIOUS STUDIES

Hydrogeological and geochemical investigations at sulfide-bearing tailings impoundments in central and eastern Canada were initiated in the 1960's in response to a growing awareness of the potentially damaging environmental effects associated with mine tailings. For example, in northeastern New Brunswick the principal concern focused on the spawning grounds of Atlantic salmon. The potential effects of the mining industry on the salmon fishery, and the steps taken to ensure acceptable river-water quality, were outlined by BELL and NANCARROW (1974) and BUSSE (1974). In conjunction with these studies, a detailed investigation of the geochemistry of an inactive tailings impoundment at the Heath Steele Zn-Pb-Cu mine in northeastern New Brunswick was conducted by BOORMAN and WATSON (1976).

Also in the 1970's, in response to concern about the disposal of low-level nuclear wastes, hydrogeologic investigations of inactive uranium mill-tailings impoundments were undertaken in the Elliot Lake area of Ontario (MOFFET and TELLIER, 1978). Subsequent investigations were extended to include detailed studies of the geochemistry of the vadose zone (SMYTH, 1981), and of the hydrogeology and geochemistry of the saturated zone of these tailings (CHERRY et al., 1980; BLAIR et al., 1980; DUBROVSKY et al., 1984a, 1984b). One of the conclusions of these studies was that the principal mechanism controlling the release and transport of radionuclides from the tailings was the oxidation of sulfide minerals contained in the tailings. Sulfide oxidation generated low-pH pore waters which enhanced the mobility of the radionuclides.

SITE DESCRIPTION AND HYDROGEOLOGIC SETTING

The Waite Amulet tailings are located approximately 20 km west of Rouyn-Noranda, Quebec, in an area of cool and humid climate. The depth of the 41 ha impoundment (Fig. 2) ranges from 2 m at the impoundment margins to more than 15 m in the centre (DAVE et al., 1986). The surface of the tailings supports a lush vegetative cover which was developed in stages from 1978 to 1981 by the addition of substantial amounts of agricultural limestone (up to 45 t/ha) and fertilizer (up to 2.2 t/ha). Runoff generated from the impoundment flows through small streams to a collection pond and water treatment facility (Fig. 2) located adjacent to the impoundment.

Although the Waite Amulet mill processed ore from ten different ore bodies, all were of the massive sulfide type and all contained between 60 and 90% sulfide minerals and magnetite. Pyrite, pyrrhotite, sphalerite and chalcopyrite were the predominant sulfides. Galena, native silver, cosalite and electrum were categorized by PRICE and BANCROFT (1948) as minor constituents of the ore. These minerals, plus others, including native bismuth, bismuthinite, tetrahedrite, stannite and cassiterite, have been observed in the tailings. The principal host rocks were andesite and rhyolite flows and breccias cut by felsic to intermediate dykes. The principal gangue minerals, as noted in the tailings, are silicates such as quartz, chlorite, muscovite, talc, feldspar and pyroxene. The major steps in the milling process were grinding, aeration and flotation

(Fig. 3). The ore was ground to about 70% minus 200 mesh. The concentration process involved the addition of chemicals, including frothing agents, flotation-enhancement and selective depressant chemicals, and pH-adjustment reagents (Table 1). Aggressive chemical reagents intended to dissolve or consume ore minerals were not used; as a consequence, the sulfide and silicate gangue minerals probably passed into the tailings impoundment relatively unaffected. The tailings and waste process-water were transported by pipeline from the mill to the tailings impoundment. The location of the discharge point was moved periodically around the southern portion of the tailings impoundment to distribute the tailings evenly. With this disposal technique, the coarser tailings should have settled near the discharge point and the finer tailings should have settled more distally. In this study, finer grain sizes and a more complex tailings stratigraphy have been observed toward the northern (distal) end of the Waite Amulet tailings.

Hydrogeologic investigations presented by DAVE et al. (1986) indicated that the tailings are underlain by 2 - 20 m of clay, which in turn is underlain by bedrock (Fig. 4). The measured hydraulic conductivity of the tailings ranged from 9.0×10^{-7} cm/s to 1.4×10^{-3} cm/s (DAVE et al., 1986). Low hydraulic conductivities were generally reported for the northern end of the impoundment, and high hydraulic conductivities for the southern end where the coarser tailings were deposited. The water table varies from near the tailings surface, to more than 5 m below the surface at the southern end of the impoundment. Horizontal and vertical hydraulic gradients indicate the pore waters within the impoundment are generally moving outward towards the

drainage ditches surrounding the impoundment. Estimated pore-water velocities range from 0.004 to 5 m/a. Higher velocities adjacent to the tailings dam have been reported (DAVE et al., 1986).

METHODS OF INVESTIGATION

The investigations conducted at the Waite Amulet site included collection and analysis of samples of the tailings solids, pore water, and pore gas. Analyses were obtained for samples collected adjacent to six piezometer nests on the top of the impoundment and at two piezometer nests on the dam face, which together represent two vertical cross-sections along the length and width of the impoundment (Fig. 4).

Tailings solids

Mineralogical analysis.

Core for mineralogical analysis was collected in sections 1 m long and about 8 cm in diameter; the core was cut into 20-cm sections, frozen at the field site, and shipped and stored frozen until ready for study.

Samples were thawed and dried at room temperature. Cores with observable special or unique features were partitioned into subsamples during the thawing process. Each of the dried samples was screened, and, when necessary, lightly crushed by hand to pass minus 36 mesh (aperture size 425 μm).

From the 69 core samples collected, 82 polished sections were prepared for mineralogical study. The tailings were rescreened to minus 270 mesh (aperture size 53 μm), and the fines rejected prior to polished-section preparation. To minimize the possible dissolution of water-soluble phases, all of the polished

sections were prepared using non-aqueous media. All polished sections were examined under reflected light, and several were also examined by scanning electron microscopy combined with energy-dispersion analysis.

Physical properties.

Bulk physical properties were determined on separate samples, which were collected with a 3.8-cm (1.5 in) soil auger adjacent to each of the 8 piezometer nests. Properties measured included bulk density, particle density, porosity, and moisture content.

Chemical analyses.

Analytical determinations were performed by the Chemical Laboratory, CANMET, for Ca, Fe and sulfate-sulfur in the water-soluble fraction, the pH of the water-leached suspension, total sulfate-sulfur, and elemental sulfur. Calcium and iron were analyzed by Atomic Absorption Spectrophotometry, and sulfate by liquid chromatography, using the water-soluble sample obtained from 2.0-g samples shaken in 100 mL of water. Total sulfate-sulfur was determined by liquid chromatography using samples digested in sodium carbonate solution. Carbonate content was determined as CO_2 by Bondar-Clegg Company Ltd. using a Coulometric automatic CO_2 analyzer.

Tailings pore-water

Pore-water samples were extracted from cores taken from the vadose zone of the tailings. Cores were collected in 7.62-cm (3 in) diameter aluminum irrigation tubing in 1 or 2 m lengths. The cores were cut into 20-cm sections

and pore-water samples were extracted using the immiscible-displacement technique described by PATTERSON et al. (1978) modified according to SMYTH (1981). This technique was used because it minimized contact between pore-water samples and atmospheric O_2, thus limiting Fe^{2+} oxidation during sample collection. Approximately 40 mL of sample were collected from each 20-cm section of core. This sample was filtered through a 0.45-μm filter, then separated into two aliquots, one acidified with 12 N HCl to a pH less than 1.0 for cation analysis, and the other left unacidified for anion analysis. Cation analysis was conducted by Atomic Absorption Spectrophotometry. Sulfate was analyzed gravimetrically by precipitation with $BaCl_2$. Chloride was analyzed by spectrophotometry. Analyses for total inorganic carbon were conducted using a Total Carbon Analyzer (Beckman Model 915). Separate subsamples were also collected for field determinations of pH (Orion Ross), Eh (Orion 96-78 platinum electrode), specific conductance, and Fe^{2+}. Ferrous iron concentration was determined with the potassium dichromate titration technique of WASER (1966).

Pore-gas analysis

The pore gas of the vadose zone of the tailings was sampled and analyzed using a modification of the technique described by REARDON and POESCENTE (1984). Narrow diameter (0.64 cm diameter) stainless steel tubes fitted with machined brass tips were driven into the tailings at depth intervals of 10 cm. Pore-gas O_2 and CO_2 concentrations were measured by directly connecting a Nova model 305LBD portable gas analyzer to each stainless steel tube. This portable meter pumps the gas over a Pb-PbO detector and through

an infra-red CO_2 gas analyzer. Oxygen concentrations were also measured in the field using a Neutronics portable O_2 analyzer. Draeger tubes were used to provide an independent field measurement of the CO_2 concentrations. To verify field analyses, gas samples were collected and stored in sealed glass bottles for analysis by gas chromatography. The lower limit of these techniques is about 0.1% O_2 and 0.3% CO_2.

Pore-water geochemical data quality analysis

The accuracy and precision of the tailings pore-water geochemistry data were assessed through charge-balance calculations as well as through analysis of blank and spike samples, replicate and split-sample analysis, and by split replicate analysis performed by an external laboratory.

Blank samples and three sets of spiked samples which contained high, moderate, and low concentrations of Al, Ca, Co, Cu, Fe, Mg, Mn, Ni, Pb and Zn were submitted with field samples for analysis. Analyses of blank samples indicated no false positive results. Analyses of spiked samples indicated that the accuracy and precision are acceptable for concentrations above the reported detection limit.

Replication of field samples from the vadose zone is limited by sample volume, and therefore only limited field duplicate analyses are available. Field replicate samples were prepared both as split replicates and as time-series replicates from an individual core. Statistical analysis of field duplicate results was conducted using the method of THOMPSON and HOWARTH (1978). The reproducibility was tested for each of the species analyzed using the reported

detection limit and a 10% level of precision. In all cases the level of reproducibility of analysis was found to be acceptable at this level of precision. The split-sample analysis variability was found to be less than the variability of the time-series samples, indicating that the spatial variability of pore-water chemistry within a single core sample is greater than the variability in analytical results.

Methods of interpretation

The geochemical data collected at the Waite Amulet field site were interpreted with the aid of the equilibrium geochemical speciation/mass-transfer model MINTEQ (FELMY et al., 1983). This geochemical equilibrium model contains an extensive data base and allows for a variety of different geochemical calculations involving aqueous, gaseous, and solid phases. The K_{sp} values used throughout this study were those incorporated in the data base of MINTEQ, which is based on the data base of the computer code WATEQ2 (BALL et al., 1979). Modifications to this data base were made according to the recommendations of NORDSTROM et al. (1984).

In this study, the degree of saturation of the pore water with respect to a mineral phase is presented as the saturation index (SI), where SI is defined as the log of the product of the aqueous activities of the mineral components (log IAP) minus the log of the equilibrium mineral-solubility product (log K_{sp}). SI values of zero indicate a system that is at equilibrium with the mineral phase, negative values indicate undersaturation, and positive values indicate supersaturation. Geochemical equilibrium calculations performed using computer

codes such as MINTEQ do not conclusively prove the presence or absence of primary or secondary solid phases, but rather provide an indication of the tendency for a reaction to occur.

RESULTS AND DISCUSSION

Characterization of the initial condition of the tailings

An important aspect of the study of the geochemistry of inactive tailings impoundments is the assessment of the initial nature of the tailings solids and pore waters as they were deposited. This initial condition, which provides the basis for all future geochemical changes in the tailings, cannot be directly assessed because the mill at the Waite Amulet site closed in 1962. The initial condition of the tailings can be inferred, however, from knowledge of the milling process and from examination of tailings solids and tailings pore waters that have not been affected by sulfide oxidation.

Tailings water samples obtained from piezometers located deep in the tailings are likely to contain concentrations of dissolved constituents similar to those of the mill process-waters discharged with the tailings. Pore-water chemical analyses from two deep piezometers, located at piezometer nest WA22 (Figs. 2, 4) were presented by DAVE et al. (1986), and in tabular form by SIWIK et al. (1987). These analyses indicated that the water near the base of the impoundment is neutral in pH, and contains high concentrations of Na, Ca, SO_4^{2-}, and lower concentrations of dissolved metals including Fe, Pb, Zn and Cu. This is similar to the composition expected for the mill process-waters (Table 1).

Geochemical equilibrium calculations performed using the geochemical computer code MINTEQ (FELMY et al., 1983) and the data presented by

DAVE et al. (1986) and SIWIK et al. (1987) indicate that the water present in the lower 4 m of the tailings attains or exceeds saturation with respect to the sulfate minerals gypsum ($CaSO_4 \cdot 2H_2O$) and jarosite ($KFe_3(SO_4)_2(OH)$), and with respect to several ferric oxyhydroxide minerals including ferrihydrite ($Fe(OH)_3$), goethite (FeOOH), and lepidocrocite (FeOOH). This water also closely approaches saturation with respect to calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$).

Core samples of tailings solids collected from the drillholes used for piezometer installation below the depth of the tailings affected by sulfide oxidation are probably representative of the original tailings. Microscopic examination of the polished sections of the core samples indicates that magnetite and the principal sulfides (pyrite and pyrrhotite) characteristically lack alteration. The grain edges of pyrrhotite, the sulfide mineral most susceptible to alteration, are typically sharp and unreplaced. In several samples, however, a few pyrrhotite grains with altered rims occur among unaltered grains. These altered pyrrhotite grains were likely oxidized while exposed on local paleosurfaces that mark interruptions in the accumulation of the tailings. That such oxidation did occur locally is evident in some cores in which rare, thin (only cm-thick), discolored oxidized layers with accompanying vegetal debris (leaves, pine needles, twigs) are straddled by tailings containing unaltered sulfides.

In summary, except for the development of thin oxidized layers at paleosurfaces, the bulk of the tailings sulfides have been unaffected by alteration. As indicated by CO_2 analysis, and confirmed by mineralogical studies, at least trace amounts of carbonate minerals, principally calcite, are present throughout

the unaltered tailings. The tailings also contain abundant euhedral crystals of gypsum, typically 0.5 to 1.0 mm long, that must have crystallized in situ. The milling reagents possibly contributed part of the Ca and SO_4^{2-}. The chemical compositions of the buried tailings pore water and the tailings solids are inferred to have been similar to those observed currently. In the absence of atmospheric or dissolved O_2, sulfide minerals were stable and the pH and Mg, Ca, SO_4^{2-} and HCO_3 concentrations were maintained at relatively constant levels by calcite-dolomite and gypsum solubility constraints.

SULFIDE OXIDATION AND ACID GENERATION

Sulfide-mineral oxidation is a complex process which occurs through reaction steps that are frequently catalyzed by sulfide-oxidizing bacteria of the Thiobacillus group. The presence of Thiobacillus ferrooxidans in the Waite Amulet tailings has been established (DAVE et al., 1986). Bacterially mediated and abiotic sulfide oxidation have been examined in several detailed studies both because of the environmental importance of these reactions and because of the economic benefits of using these reactions in ore processing. Extensive reviews of sulfide-mineral oxidation mechanisms have been presented by LUNDGREN and SILVER (1980), LOWSON (1982), and NORDSTROM (1982).

In the Waite Amulet tailings the most abundant sulfide minerals are pyrite and lesser amounts of pyrrhotite. The oxidation of pyrite, by dissolved oxygen or Fe^{3+}, is typically described as:

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

or

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$

Reaction 2 is the primary mechanism of sulfide oxidation at pH conditions of less than 4 (NORDSTROM, 1982). In both reaction (1) and (2) atmospheric oxygen is the ultimate oxidant. Equation (1) indicates that Fe^{2+}, SO_4^{2-} and H^+ are generated at a 1:2:2 ratio. The Fe^{2+} generated by pyrite oxidation may be further oxidized, hydrolyzed, and precipitated as ferric hydroxide

($Fe(OH)_3$) through the reaction

$$2Fe^{2+} + 1/2O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 4H^+ \quad (3)$$

Reaction (3) generates an additional two moles of H^+ for each mole of pyrite oxidized, resulting in a pyrite:H^+ ratio of 1:4. Frequently, in tailings systems, reaction (1) and reaction (3) are decoupled. Pyrite oxidation (reaction 1) occurs near the tailings surface, and the Fe^{2+} released, which is relatively mobile under low-pH to neutral-pH conditions, is transported by infiltrating recharge water along the tailings water-flow path, ultimately discharging to a surface water body. The result is the oxidation of Fe^{2+} through reaction (3), and the generation of H^+ in streams and lakes adjacent to tailings impoundments.

Evidence of sulfide oxidation reactions in the Waite Amulet tailings are the depletion of sulfide minerals in the near-surface zone of the tailings, and the abrupt decline in the gas-phase O_2 concentration at the zone of active oxidation. Based on microscopic studies, the degree of the alteration intensity of the Waite Amulet tailings was classified on a relative scale of 0 to 10 as described in Table 2. Profiles of gas-phase O_2, CO_2 concentrations, and sulfide alteration versus depth for the eight drill-sites studied are presented in Figure 5. The intensity of sulfide oxidation in these profiles shows a decrease that corresponds closely to the abrupt decline in the gas-phase O_2 concentration.

Mineralogical analyses of cores from the Waite Amulet site show a progressive downward decrease in alteration intensity. At the southern end of the impoundment, the progression is interrupted by a well-defined zone of paleosurface oxidation. For the impoundment as a whole the oxidation profiles can be

generalized into three zones: a sulfide-depleted zone, characterized by strongly oxidized tailings, an intermediate zone characterized by moderate to weak alteration and marcasite replacement of pyrrhotite, and an unaltered zone where the tailings show negligible oxidation.

In the upper sulfide-depleted zone only trace remnants of pyrite and chalcopyrite can be found, the bulk of the sulfides having been oxidized and replaced. The principal alteration minerals are goethite, and other iron oxyhydroxides that include lepidocrocite and ferrihydrite. The observed order of sulfide mineral removal follows the order generally observed for sulfide-mineral susceptibility to microbial oxidation (Table 13.7, BROCK et al. 1984). Pyrrhotite, the most susceptible of the common sulfides to microbial oxidation, is typically completely replaced throughout the sulfide-depleted zone. In the intermediate zone pyrrhotite has been strongly altered but not obliterated. Initial alteration of pyrrhotite is evident from partial replacement by marcasite and sulfates along grain boundaries (Fig. 6) and progressive replacement of these phases by goethite and lepidocrocite to form ferric oxyhydroxide atolls around pyrrhotite grains (Fig. 7). Similar oxidation characteristics have been noted in heap-leach piles and in naturally oxidizing waste-rock dumps.

Modelling sulfide oxidation reactions

Recognition of sulfide oxidation characteristics has lead to the development of series of mathematical models which are based conceptually on sulfide oxidation reactions occurring at the surface of a shrinking core of sulfide mineral within an oxide reaction rim. In these models, which have been sum-

marized by DAVIS and RITCHIE (1986), the rate of sulfide oxidation is controlled by diffusion of the oxidant (O_2(g) or Fe^{3+}) through the oxide reaction-rim to the sulfide surface. Initially, these models were developed to describe sulfide oxidation in heap-leach ore processing. During the heap-leach process the oxidant is continuously replenished through leach-liquor recirculation and the rate of sulfide oxidation can be assumed to be controlled solely by transport and reaction mechanisms within particles. For tailings and waste-rock piles undergoing natural oxidation, the rate of sulfide-mineral oxidation may also be controlled by the supply of oxidant into the system.

A series of mathematical models based on the assumption that the supply of oxygen to the oxidizing particles is controlled by diffusion through the pore space of the tailings, coupled with diffusion into the particles, to a moving reaction front has recently been developed (DAVIS and RITCHIE, 1986; DAVIS et al., 1986; DAVIS and RITCHIE, 1987). The simplest of these models is an approximate analytical solution (DAVIS and RITCHIE, 1986). This model assumes that all sulfide particles within the waste are equally reactive regardless of mineralogy, are spherical, of one size, and that a single diffusion coefficient can be assigned to the entire thickness of unsaturated tailings. Given these assumptions, the solution reduces to a series of easily solved equations. All of the parameters required to solve these equations can be measured from field samples.

The equations that form the basis for this approximate analytical solution can be written as

$$u(x,t) = 1 - x\frac{\sqrt{\beta}}{[1 + \sqrt{\beta}\, X]}$$

$$0 \leq z \leq X(t) \tag{4}$$

$$u(z,t) = \frac{\exp(-\sqrt{\beta}(z-X))}{[1+\sqrt{\beta}\,X]}$$

$$X(t) \leq z \leq 1 \tag{5}$$

where:

$$\beta = 6\gamma\, D_2(1-p)L^2/(D_1 a^2) \tag{6}$$

t = *dimensionless time* (t^*/τ_4)

t^* = *time* (s)

t_c = *dimensionless time to react a particle at the tailings surface* (t_0)

u = *dimensionless oxygen concentration*

z = *dimensionless depth* (z^*/L)

z^* = *depth* (m)

$X(t)$ = *dimensionless depth of planar moving front*

$X^*(t)$ = *position of planar moving front within the dump* (m)

$$\tau_4 = L^2 \epsilon \rho s/(D_1 u_o) \tag{7}$$

and $X(t)$ can be found through solution of the transcendental function

$$t = t_c + \frac{X^2}{2} + t_c \sqrt{\beta}\, X \tanh \sqrt{\beta}\,(1-z) \tag{8}$$

The parameters required to solve these equations are:

D_1 = *diffusion coefficient within the pore space of the dump* $(m^2 S^{-1})$

D_2 = *diffusion coefficient within the particles* $(m^2 s^{-1})$

p = *porosity of the tailings*

u_o = *initial oxygen concentration at the tailings surface* $(kg\ m^{-3})$

L = *total thickness of the tailings*

a = *particle diameter*

ϵ = *mass of oxygen used per mass of sulfur in the oxidation reaction*

ρ_s = *density of sulfur in the tailings* ($kg\ m^{-3}$)

γ = *proportionality constant encompassing both Henry's Law and the gas law*

Of these parameters, D_2, u_a, L, a, ϵ, ρ_s, and γ can be assumed constant for the Waite Amulet tailings. The assigned constant values for each of these parameters is presented in Table 3. Of the remaining parameters, p was calculated directly from field measurements, and D_1 was estimated from field measurements using the modification to the estimation method proposed by MILLINGTON and SHEARER (1971) recommended by MAGNUSSON and RASSMUSON (1984), and using the estimation technique proposed by REARDON and MODDLE (1985).

Of the eight oxygen-concentration profiles measured at the Waite Amulet site, five (WA2, WA8, WA20, WA21, WA24) were not considered acceptable for comparison with O_2 profiles predicted using the model of DAVIS and RITCHIE (1986). Profiles WA20 and WA21 were measured on the benches of the impoundment and were subjected to compaction during dam construction. Profiles WA2 and WA8 were saturated to within 20 cm of the tailings surface, and the profiles contained fewer than 2 data points. At profiles WA8 and WA24 a clay layer, 20-40 cm thick, was placed over the tailings during the vegetation program. For the remaining three sites (WA11, WA17 and WA22) the parameters D_1 and p were calculated from field measurements averaged over the upper 40 cm of the tailings, the depth currently affected by sulfide

oxidation. The field data and the calculated parameters are presented in Table 4.

Measured and calculated O_2 profiles are presented in Figure 8. The latter represent visual best-fit' profiles obtained by varying D_1 while maintaining all other parameters constant. The D_1 values used to obtain this best fit (Table 4) are within one order of magnitude of the calculated D_1 values.

The oxygen diffusivity (D_1) is strongly dependent on the temporally variable moisture content of the tailings. The moisture content and O_2-concentration measurements presented in this paper represent single measurements made in late November, after the autumn rains, when the moisture content of the upper tailings was high. Considering the uncertainties in the parameter estimations and the depth averaging of the parameters, the agreement between the oxygen diffusion coefficient, D_1, calculated using the method of MILLINGTON and SHEARER (1971), the method of REARDON and MODDLE (1985) and that inferred from the analytical solution of DAVIS and RITCHIE, is close.

A notable difference between the measured and calculated O_2 profiles is that the analytical solution does not simulate the concave-upward portion of the O_2 profile measured at piezometer nest WA22. This may be a consequence of assuming a constant diffusion coefficient in the pore space of the tailings (D_1). The moisture content of the tailings generally increases with increasing depth, and would result in a greater than average diffusion coefficient and thus greater oxygen penetration near the tailings surface.

The model presented by DAVIS and RITCHIE (1986) can be used to estimate $X(t)$, the depth of a moving planar front above which all the sulfide has oxidized. The horizontal dashed line on the profiles for WA11, WA17 and WA22 in Figure 8 indicates the calculated depth of this plane. The calculated depth corresponds closely to the observed decrease in sulfide alteration index at piezometer nests WA17 and WA22. The agreement is not as good at piezometer nest WA11. This may reflect inadequacies of the model or parameter selection, or may result from enhanced oxidation due to tillage of the tailings during the revegetation program.

The zone between the depth of the plane of complete sulfide oxidation and the depth of complete O_2 depletion is the zone of active sulfide oxidation. This is analogous to the zone of intermediate oxidation identified in mineralogical analysis. Figure 9 presents three predicted profiles of O_2 concentration versus depth for varying oxygen diffusivities and the depth of the plane of complete oxidation, $X^*(t)$, for each case. Examination of these profiles indicates that the rate of sulfide-mineral depletion is greatest where the oxygen diffusivity is largest (lowest moisture content). The profiles also indicate that the thickness of the intermediate zone increases with increasing O_2 diffusivity. This is in general agreement with mineralogical observations. Where the tailings are fine-grained and the water table is shallow, leading to a low O_2 diffusivity (WA2 and WA8), the intermediate zone is thin to absent; where the tailings are coarse and the water table is deep, leading to a higher O_2 diffusivity (WA17 and WA22), the intermediate zone is much thicker. A similar relationship between the oxidation profile and the tailings grain size and moisture con-

tent was recognized by SMYTH (1981) at the Nordic Mine uranium-tailings impoundment near Elliot Lake, Ontario.

Finally, the model of DAVIS and RITCHIE (1986) can be used to estimate the time required to oxidize the total sulfide mineral content of the vadose zone (t_d) if the parameter L (total thickness) is set equal to the thickness of the vadose zone, through the equation

$$t_d = \frac{L^2 \epsilon \rho s}{(D_1 u_o)} \tag{9}$$

The time for complete oxidation of all the sulfides at the piezometer nests WA11, WA17, and WA22 was calculated using the three D_1 values and assuming the vadose zone extends from the tailings surface to the water table position shown in Figure 5. These calculations assume a constant sulfide content and $O_2(g)$ diffusivity with depth, and consider $O_2(g)$ as the only significant oxidant. The results of these calculations, presented as a range of values in Table 4, indicate that sulfide oxidation in the vadose zone of the tailings will continue for several centuries.

SOLUBILITY CONTROLS ON PORE-WATER CONCENTRATIONS AND THE FORMATION OF SECONDARY MINERALS

The principal environmental problems associated with the sulfidic tailings at the Waite Amulet site are the potential for acid generation and the increased mobility of Cu, Pb, Zn, Cd and Co under low-pH conditions. Understanding the geochemistry of the major ions in solution, Ca, Fe, K, Mg, Na, SO_4^{2-} and HCO_3^-, is important because Fe^{2+} is the principal potential source of acidity associated with tailings pore waters, and because chemical reactions between the major ions can lead to the development of a well-buffered geochemical system. The activities of the heavy metals are controlled by this system. Therefore, knowledge of the chemistry of the major ions is fundamental both to understanding and predicting the potential acidity associated with tailings pore waters, and to understanding the distribution and mobility of the heavy and trace metals.

Acid neutralization processes

As sulfide-oxidation reactions proceed at the tailings surface, the mobile reaction products are gradually displaced downward through the vadose zone of the tailings toward the water table. Equation 1 indicates that pyrite oxidation reactions generate 2 moles of H^+ for each mole of Fe^{2+} released. Comparison of the profiles of pH versus depth (Fig. 10a) with the Fe^{2+} profile (Fig. 10b)

indicates that high concentrations of Fe^{2+} generated by sulfide oxidation are present throughout the vadose zone, whereas the zone of low-pH conditions is restricted to shallow depths. This difference is attributed to the effect of H^+-consuming reactions occurring in the vadose zone. Mechanisms of H^+ consumption involved in tailings pore-water neutralization include dissolution of carbonate minerals, dissolution of aluminosilicate minerals, dissolution of iron and aluminum hydroxide minerals, and H^+ adsorption on mineral surfaces (DUBROVSKY et al., 1984a).

Analyses for carbonate minerals were done on samples of tailings solids collected from 1 and 2 m below the tailings surface, the zone not affected by carbonate addition during revegetation. Of fourteen samples analyzed, only two (0.3 m and 0.5 m at WA8) contained a carbonate content above detection (0.5 wt% $CaCO_3$).

Carbonate-mineral dissolution and acid neutralization can be represented by the reaction for calcite

$$2\,H^+ + CaCO_{3(s)} \rightarrow Ca^{2+} + H_2CO_3^* \qquad \text{for } pH \leq 6.0 \qquad (10)$$

This reaction increases pore-water pH levels, and H_2CO_3 and Ca^{2+} concentrations. Dissolution of dolomite increases both Ca^{2+} and Mg^{2+} concentrations. Profiles of measured Ca and Mg concentrations are presented in Figure 10c. The concentrations of Ca throughout the tailings range between 400 and 600 mg/L, and are relatively constant with depth and location. The Mg concentrations are more variable, possibly reflecting differences in the Mg content of the carbonate minerals initially present in the tailings and the carbonate minerals added during the revegetation program. Above the water table, high CO_2 con-

centrations were measured in the gas phase (Fig. 5). High gas-phase CO_2 concentrations probably arise from degassing of CO_2 generated by carbonate-mineral dissolution. Pore-water H_2CO_3 concentrations were measured as total inorganic carbon (TIC) several weeks after sample collection. During the period between sample collection and analysis there was potential for Fe^{2+} oxidation and precipitation as $Fe(OH)_3$, resulting in H^+ generation and carbon loss through CO_2 degassing reactions. This leads to an unavoidable uncertainty in pore-water H_2CO_3 concentrations.

Geochemical equilibrium calculations conducted using MINTEQ and the water-chemistry data indicate that pore water throughout the vadose zone is undersaturated with respect to calcite, dolomite and siderite. Carbonate-mineral analyses indicate that the carbonate minerals initially present in the vadose zone have been extensively depleted. Carbonate minerals that remain in the upper 50 cm of the tailings probably resulted from the addition of limestone during the revegetation program. Undersaturated conditions where carbonate minerals are present in the vadose zone suggest that these minerals are dissolving and will continue to dissolve until the pore water reaches saturation with respect to these minerals or until these minerals are completely depleted. Generally, carbonate-mineral dissolution reactions are considered to be rapid (DUBROVSKY et al., 1984a).

Analysis of the tailings pore-water samples indicates that the pore water near the tailings surface contains high concentrations of dissolved aluminum. High Al concentrations have previously been reported in waters affected by acidic drainage from sulfide oxidation occurring in natural soils (VAN

BREEMAN, 1973), in surface waters affected by acid mine drainage (NORDSTROM, 1986), and in tailings pore waters (SMYTH, 1981; DUBROVSKY et al., 1984a). In all of these cases, the increased concentration of Al has been attributed to aluminosilicate-dissolution pH-buffering reactions. Results from the Waite Amulet site, where the only identifiable source of the high dissolved Al concentrations (up to 800 mg/L) is the dissolution of aluminosilicate minerals, are in agreement with these previous studies.

Although aluminosilicate dissolution reactions lead to an increase in pore-water pH, a large source of potential acidity remains because Al may reprecipitate as hydroxide minerals (e.g. $Al(OH)_3$) which will consume base and lower the pH. In addition to buffering the tailings pore-water pH and releasing Al and SiO_2 to solution, aluminosilicate dissolution generally releases major cations (Na, K, Ca, Mg, Fe^{2+} and Mn^{2+}) to solution. In the high-Fe, SO_4^{2-} environment present in the tailings, these cations play an important role in the formation of secondary mineral phases such as K and Na jarosites and gypsum.

The major ions

Iron is the principal cation in all of the pore-water samples collected from the vadose zone at the Waite Amulet site. Iron speciation is dependent on both pH and redox potential (Eh). Iron speciation was estimated using the measured Fe^{2+} concentration, the measured oxidation-reduction potential (Eh), and the Nernst equation:

$$Eh = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad (11)$$

Several studies (BOORMAN and WATSON, 1976; NORDSTROM, 1982; DUBROVSKY et al., 1984a and 1984b) have indicated that Eh measurements are a useful tool in interpreting the geochemistry of waters affected by acid mine drainage. Measurements of oxidation-reduction potential are difficult and susceptible to error. The limitations of Eh measurements have been documented by WHITFIELD (1974).

The Fe^{3+} activities calculated from the measured Eh values ranged from 1×10^{-20} to 1×10^{-9} molal. This is much lower than the measured Fe^{2+}, and is consistent with the observation that the variation in the measured Fe^{2+} concentration is generally greater than the difference between the Fe^{2+} and Fe_T determinations. The Fe^{3+} concentrations determined from the Eh measurements were used in MINTEQ to calculate the degree of saturation with respect to Fe^{3+} and Fe^{2+} oxyhydroxide and sulfate minerals.

Profiles of SI for the ferric oxyhydroxide phases $Fe(OH)_3$, goethite, and lepidocrocite versus depth for six of the locations (WA2, WA8, WA11, WA21, WA22 and WA24) are presented in Figure 11. At shallow depths all of these profiles are calculated to be undersaturated with respect to these three ferric oxyhydroxide minerals. This is the zone of sulfide depletion and low-pH conditions where ferric oxyhydroxide minerals previously precipitated may be dissolving. Below this zone, SI values rise. At four locations (WA11, WA21, WA22 and WA24), the pore waters are very close to saturation with respect to $Fe(OH)_3$, and are supersaturated with respect to goethite and lepidocrocite. At the remaining two locations (WA2 and WA8) the pore water is undersaturated with respect to $Fe(OH)_3$, and is very close to saturation with respect to both

goethite and lepidocrocite. LANGMUIR and WHITTEMORE (1971) suggested that the first ferric precipitates to form in streams affected by acid mine drainage are ferric hydroxide ($Fe(OH)_3$) and poorly crystalline goethite. These more soluble ferric hydroxides preferentially dissolve and transform into the thermodynamically more stable crystalline goethite and lepidocrocite with time. The two sampling locations where goethite and lepidocrocite are at saturation (WA2 and WA8) are in the north-central portion of the impoundment where the tailings are fine-grained, pore-water velocities are low and pore-water residence times are long.

Mineralogical analysis and X-ray diffraction patterns of the tailings solids confirm the presence of the secondary goethite, lepidocrocite, ferrihydrite, and amorphous iron oxides. In the sulfide-depleted zone, goethite and lepidocrocite coexist as intimate mixtures that have replaced individual grains of pyrrhotite. Ferrihydrite is metastable with respect to goethite and hematite (LANGMUIR and WHITTEMORE, 1970; TORRENT and GUZMAN, 1982; TORRENT et al., 1982), and lepidocrocite is metastable with respect to goethite.

Mineralogical studies of the tailings indicate an abundance of iron and calcium sulfate minerals, and the presence of small amounts of elemental sulfur. The most common Ca^{2+}, Fe^{3+} and Fe^{2+} sulfates are gypsum, K-jarosite, and sulfates of the type $FeSO_4 \cdot nH_2O$, respectively. Calculations indicate high degrees of supersaturation with respect to jarosite ($KFe_3(SO_4)_2(OH)_6$). High degrees of supersaturation with respect to jarosite in waters affected by acidic sulfate-rich drainage has been previously reported by others (VAN BREEMAN, 1972; NORDSTROM, 1982; DUBROVSKY et al., 1984a, 1984b). Energy-

dispersion analysis indicates that the jarosite is normal potassium jarosite; minor variations observed in X-ray patterns of the jarosite probably represent substitution of Na^+ for K^+. The most probable sources of potassium are K salts in the initial mill reagents, K included in fertilizers added during the revegetation program, and K derived from dissolution of K-feldspar contained in the silicate gangue.

Chemical analyses of the tailings have shown that, of the total sulfate, that part which is insoluble in water is a good measure of the jarosite content. The insoluble sulfate content is plotted versus depth in Figure 12. These profiles indicate up to 2.5 wt% jarosite in the sulfide-depleted zone. At several sites, local accumulations of jarosite are extensive enough to lead to the development of thin discontinuous layers of cemented tailings. These layers probably represent a primitive stage in the development of hardpan. Layers of cemented tailings have been reported from other inactive tailings impoundments in Canada and the northern United States (BOORMAN and WATSON, 1976; McSWEENY and MADISON, 1988; BLOWES et al., 1988). BLOWES et al. (1988) reported an abrupt decrease in gas-phase CO_2 concentrations upwards across a continuous layer of ferrous sulfate and hydroxide minerals in an abandoned tailings impoundment at the Heath Steele mine in New Brunswick, Canada, and attributed this decline to the low CO_2 diffusivity of the cemented tailings.

Small amounts of ferrous sulfates ($FeSO_4 \cdot nH_2O$) have been noted in mineralogical studies of the dried tailings. The pentahydrate (siderotil) and hexahydrate (ferrohexahydrite) form white blooms, and the heptahydrite (melanterite)

crystallizes abundantly on moistened cores. It is possible that these ferrous sulfate solid phases, as well as the tetrahydrate (rozenite, $FeSO_4 \cdot 4H_2O$) and the monohydrate (szomolnokite, $FeSO_4 \cdot H_2O$) may form as ephemeral precipitates on the sun-baked surface crusts. Geochemical equilibrium calculations indicate that the tailings water is consistently undersaturated with respect to szomolnokite ($SI \leq -2.26$) and approaches but does not attain saturation with respect to melanterite at any of the points sampled ($SI \leq -0.839$). Precipitation of ferrous sulfate minerals does not appear to provide a significant solid-phase control on pore-water Fe^{2+} concentrations.

The most abundant sulfate mineral in the tailings is gypsum. Geochemical equilibrium calculations indicate that all water samples collected are at or near saturation with respect to gypsum ($-0.20 < SI < +0.20$). Probable sources of the Ca are the milling reagents, and the dissolution of carbonate minerals and aluminosilicate minerals. The SO_4^{2-} was probably derived from a combination of the initial mill process-water and from sulfide oxidation reactions.

The amount of $CaSO_4$ in the tailings solids was determined by chemical analysis for Ca and SO_4^{2-} in water-soluble fractions of the samples. Variation in wt% $CaSO_4$ with depth is presented in Figure 13. These profiles indicate that gypsum is present throughout the vadose zone, is most abundant near the tailings surface or in the zone of sulfide oxidation, and is lowest near the base of the profiles. This trend suggests that SO_4^{2-} present in the initial mill-process water, and SO_4^{2-} generated by sulfide oxidation, have both contributed to the formation of gypsum, the precipitation of which represents an important solid-phase control on pore-water SO_4^{2-} and Ca concentrations.

The measured high Al concentrations represent a significant source of acidity because of the potential formation of aluminum hydroxide minerals. The detection limit for Al analysis in this study was relatively high, generally 50 mg/L. The majority of Al concentrations in excess of 50 mg/L were recorded from samples obtained from the low-pH zone near the tailings surface. Only one sample with a pH > 5.0 contained more than 50 mg/L Al. NORDSTROM (1982) suggested that Al concentrations in waters with pH < 5.3 may be controlled by precipitation of basic aluminum sulfate minerals. Calculated SI values for the aluminum sulfate-hydroxide minerals jurbanite ($AlSO_4OH$), basaluminite ($Al_4(SO_4)(OH)_{10}$), and amorphous aluminum hydroxide ($Al(OH)_3$) indicate varying degrees of saturation and supersaturation for each of these minerals. A plot of log (Al) versus pH, for a constant SO_4^{2-} activity of 10^{-2}, indicates that log (Al) is relatively constant (mean = 3.580, S.D. = 1.214) and independent of pH (Fig. 14). This suggests that none of these solid phases represent a significant solid-phase control on pore-water Al concentrations under low-pH conditions. DUBROVSKY et al. (1984a) found that Al activity seemed to be independent of pH for pore waters with pH < 3.5 in the Nordic mine tailings near Elliot Lake, Ontario. NORDSTROM and BALL (1986) reported that Al behavior in acidic mine-drainage water samples was conservative. Both of these studies agree with the current observation that, under low-pH conditions, these aluminum hydroxy-sulfate minerals do not provide an effective solid-phase control on pore-water Al concentrations. Secondary aluminum-bearing solid phases were not detected in the mineralogical study.

The metals

The preceding discussion indicates that, below the zone of sulfide oxidation, the precipitation and dissolution of a series of solid phases control the concentrations of the major ions. These reactions have lead to the development of a relatively well-buffered geochemical system. The geochemical behavior of Cr, Co, Cu, Mn, Ni, Pb and Zn is controlled by this system.

The distribution and relative mobility of metals in weathered sulfide terrains has been studied extensively by economic geologists investigating supergene enrichment of massive sulfide orebodies. The geochemical mechanism controlling the distribution of metals in the Waite Amulet tailings can be compared to the mechanisms controlling supergene enrichment processes.

Profiles of the concentration of the metals Co, Mn, Cu, Ni, Pb and Zn versus depth are presented in Figure 10. The concentration and mobilities of these metals generally follow the order Fe = Mn $\geq$ Zn > Ni $\geq$ Co > Pb > Cu. This order is similar to the order Co = Ni > Zn > Pb > Cu observed by DUBROVSKY (1986) at the Nordic Main tailings impoundment near Elliot Lake, Ontario. MANN (1983) reported the relative order of mobility Zn > Cu > Pb in weathered massive sulfide environments at pH < 6.1. The mobility of these metals after they are released by sulfide oxidation is controlled by precipitation-dissolution reactions, coprecipitation reactions, solid-solution substitutions, and adsorption-desorption reactions. Each of these types of reactions appears to play an important role in the movement of metals in the Waite Amulet tailings.

The concentration of Pb reaches a maximum of 5.1 mg/L at 0.9 m below the surface at WA21. Lead concentrations approach saturation with respect to anglesite ($PbSO_4$) at several points in the impoundment, and attain saturation near the tailings surface at WA21. Possibly because of the small quantity, anglesite was not isolated by mineralogical study of tailings core samples. Anglesite is a common secondary mineral associated with weathered sulfide environments. Anglesite attributed to secondary mineral precipitation has been identified in an inactive base-metal tailings impoundment in northeastern New Brunswick by BOORMAN and WATSON (1976), and DUBROVSKY (1986) reported that most of the tailings pore-water samples with pH > 4.5 collected from an inactive uranium-tailings impoundment in Elliot Lake were saturated or supersaturated with respect to anglesite. Anglesite is an important alteration mineral in weathered Pb-bearing sulfide ore bodies (GUILBERT and PARK, 1986).

Copper occurs at concentrations higher than that of Pb and seems to be less mobile than Pb at the Waite Amulet site. The tailings pore waters are consistently undersaturated with respect to copper sulfate or carbonate minerals. Mineralogical study has shown that traces of covellite (CuS) are present. Covellite was also identified by BOORMAN and WATSON (1976), in an inactive tailings impoundment at the Heath Steele mine in New Brunswick. Covellite replacement of pyrrhotite and sphalerite (ZnS) can be expressed by:

$$Cu^{2+} + FeS \rightarrow Fe^{2+} + CuS \qquad (12)$$

$$Cu^{2+} + ZnS \rightarrow Zn^{2+} + CuS \qquad (13)$$

This latter reaction removes Cu^{2+} from solution and releases Zn^{2+}. At all locations where Cu concentrations show an abrupt decrease, the concentrations of Fe^{2+} and Zn^{2+} are high enough to account for the decrease in Cu concentration. KRAUSKOPF (1968) noted that replacement reactions are favored for metals that have relatively insoluble sulfides and relatively soluble secondary minerals. Of the metals commonly encountered in tailings impoundments, Ni, Cu and Ag fit these criteria.

The concentrations of Cu in the tailings pore water are plotted versus depth in Figure 10e and in Figure 15. As for iron, copper speciation was calculated using the measured Eh and the Nernst equation. These calculations suggest that Cu^{2+} is the dominant Cu species in the water present in the upper 1 to 2 m of the tailings. Also on Figure 15, the solid-phase elemental sulfur content is plotted versus depth. At the Waite Amulet site, elemental sulfur contents range from below 0.01 wt % to more than 1.0 wt %. Generally the highest elemental sulfur contents occur near the zone of active oxidation. Each of the profiles in Figure 15 shows an abrupt decrease in Cu concentration at a depth that corresponds closely with an increase in solid-phase elemental sulfur content. Geochemical equilibria calculations, assuming the calculated Cu speciation and assuming the tailings water is in equilibrium with solid-phase elemental sulfur, were conducted. These calculations suggest that the water near the tailings surface, where Cu concentrations and elemental sulfur contents are low, is undersaturated with respect to covellite. As depth, Cu concentration, and elemental sulfur content increase, the tailings water approaches or exceeds saturation with respect to covellite. At the depth of the maximum Cu

concentration, at several of the locations sampled, geochemical calculations suggest that the tailings waters are saturated or supersaturated with respect to covellite and undersaturated with respect to sphalerite. The abrupt decrease in dissolved Cu concentrations below the zone of covellite formation suggests that this reaction is an important solid-phase control of Cu concentrations in tailings environments.

Nickel concentrations are low throughout the impoundment. The maximum Ni concentration was 15 mg/L from 1.5 m below ground surface at WA22. In the description of the ore mineralogy presented by PALMER (1957), the presence of discrete nickel-bearing sulfide minerals was not mentioned. The Ni present in the tailings pore water could have originated as a solid-solution element in the iron sulfides or oxides, or in the host-rock silicates, but is most likely to have been derived from pyrrhotite.

NICKEL et al. (1974) described supergene alteration and secondary mineral formation in a nickel-rich pyrrhotite-pentlandite ore body in western Australia. The principal nickel-bearing non-sulfide secondary minerals reported were the carbonates, gaspeite ($(Ni,Mg,Fe)CO_3$) and nickeloan magnesite, and the nickel sulfate minerals, retgersite ($NiSO_4 \cdot 6H_2O$), nickel hexahydrite ($NiSO_4 \cdot 6H_2O$), and morenosite ($NiSO_4 \cdot 7H_2O$). MINTEQ calculations indicate that the pore water throughout the tailings is undersaturated with respect to all secondary Ni carbonate, sulfate, and hydroxide minerals. Neither violarite (Ni_2FeS_4) nor any of the Ni-bearing secondary minerals were detected by mineralogical analysis. Therefore, the most likely mechanisms limiting the pore-water Ni concentrations, if any, are adsorption and coprecipitation reactions.

Adsorption and coprecipitation reactions can lead to the removal of dissolved species from solution at concentrations below the solubility limits of discrete mineral phases. In a complex and active geochemical system, as is present in the vadose zone of the Waite Amulet tailings, it is difficult to distinguish between adsorption and coprecipitation reactions. DUBROVSKY (1986) suggested that adsorption may be an important process controlling the mobility of the heavy metals in the pore waters of the Nordic uranium mill tailings near Elliot Lake. Data presented by KINNIBURG et al. (1976) show the extent of Ni removal by adsorption reactions increases with increasing pH. THORNBER (1983) conducted a series of experiments to determine the extent $Fe(OH)_3$ precipitates can accumulate heavy metals in the gossans of weathered massive-sulfide ore bodies. The results of these experiments demonstrated that coprecipitation reactions can effectively remove significant concentrations of Ni, Co, Cu, Pb and Zn from solution. LECKIE et al. (1980) have shown that adsorption/coprecipitation with $Fe(OH)_3$ can be used to remove Cd, Cu, Zn, As, and Se from waste-water streams. The similarity between the tailings pore water and the systems studied by THORNBER (1983) and LECKIE et al. (1980) suggests that adsorption/coprecipitation reactions probably play an important role in controlling the concentrations of Ni, Co, Pb and Zn in the Waite Amulet tailings.

Cobalt is similar in mobility to Ni at all of the piezometer nests sampled. Cobalt is a sulfophile element that can substitute into either the pyrite or pyrrhotite lattice. As with Ni, Co present in the tailings pore water probably originated in the sulfide minerals. The maximum Co concentration (8.9

mg/L) was obtained from 1.10 m below the tailings surface at location WA21. DUBROVSKY (1986) noted that the geochemical behavior of Co in the pore waters of the Nordic Main tailings was similar to that of Ni, and suggested that Co concentrations at that site were controlled by adsorption reactions. It is probable that the Co concentrations at the Waite Amulet site are also controlled by adsorption/coprecipitation reactions.

Zinc is one of the most mobile of the heavy metals in the Waite Amulet tailings and occurs at the highest concentrations (up to 250 mg/L). Zinc is released to the tailings almost wholly by the oxidation of sphalerite (ZnS). As with Ni, the tailings pore waters do not reach saturation with respect to any discrete Zn-bearing secondary minerals. It is likely, therefore, that adsorption or coprecipitation reactions also control the Zn concentrations. The extent of Zn removal by adsorption onto metal oxide surfaces increases with increasing pH. KINNIBURG et al. (1976) indicated extensive Zn adsorption onto Fe and Al oxide gels above pH = 5.5. THORNBER (1983) indicated that coprecipitation with ferric hydroxides may also play an important role in controlling Zn mobility in weathered sulfide environments. Compositions determined in the mineralogical study suggest that at least some Zn and Cu are coprecipitated with the ferrous sulfate minerals.

Manganese is approximately equal to Fe^{2+} in mobility, and, like iron, is a multivalent metal. Calculations using the measured Eh value and the Nernst equation indicate that the dominant manganese species in the pore water is Mn^{2+}. The only manganese-bearing solid phase that approaches saturation is rhodocrosite ($MnCO_3$) (Max SI=-1.451). Rhodocrosite was not isolated by min-

eralogical analysis. As with Ni, Co and Zn, adsorption/coprecipitation reactions are probably the most important controls on the pore-water Mn concentration.

Chromium, which, unlike the other metals, may have been added during the milling process, reaches maximum concentrations about 4 mg/L. Chromium may have originated in magnetite, and been released through magnetite oxidation and dissolution, or Cr may have been added during ore processing. Dichromate, either in the potassium or sodium form, is commonly added during the milling of sulfide ores to depress galena during the zinc-flotation process (OKADA and MAJIMA, 1971). PALMER (1957) does not indicate that dichromate was used in the Waite Amulet mill at that time and noted that a special Cu-Ag-Au concentrate was floated directly from the rod mill discharge to prevent galena contamination of zinc concentrates. Dichromate, however, may have been used at other periods during the life of the mill. In the milling water, dichromate reacts with and may be retained on the surfaces of galena (OKADA and MAJIMA, 1971). Sulfide-oxidation reactions in the tailings impoundment may subsequently release Cr to the tailings pore water. In the milling process, or in the tailings impoundment, the Cr^{6+} may be reduced to Cr^{3+} either by reaction with pyrite or with dissolved Fe^{2+}. The Cr^{3+} oxidation state is, therefore, likely to account for the bulk of the Cr in the tailings pore water.

PROGNOSIS

The field studies conducted at the Waite Amulet site have provided considerable information which can be used to predict the future geochemical evolution and environmental impact of these tailings. Oxidation reactions have extensively removed sulfide minerals from the uppermost part of the tailings and have generated low-pH conditions and high concentrations of SO_4^{2-}, Fe^{2+} and other metals. Predictions based on the field data and the approximate analytical solution of DAVIS and RITCHIE (1986) suggest that pyrite oxidation in the vadose zone will continue for at least five centuries. This estimate is probably conservative as it neglects the effects of O_2 diffusion below the water table and the effects of dissolved Fe^{3+} oxidation of sulfide minerals. Considering the groundwater flow velocities reported by DAVE et al. (1986), the Fe^{2+} generated by sulfide oxidation reactions should continue to move down through the tailings along groundwater flow paths for many centuries after the sulfide content of the vadose zone has been depleted. This will result in the generation of acidity, in surface water bodies adjoining the tailings, for more than a thousand years.

Low-pH conditions are currently restricted to the upper zone of the tailings. This is attributed to H^+-consuming mineral-dissolution reactions within the vadose zone. The principal pH-buffering mechanism seems to be carbonate dissolution. As the carbonate buffering capacity in the vadose zone is exhausted, the zone of low-pH water will expand to occupy a more extensive portion

of the tailings impoundment. The combination of equations (1) and (10) describes pyrite oxidation and acid neutralization by carbonate dissolution. At pH < 6.0, one mole of calcite is required to neutralize the H^+ produced by the oxidation of one mole of pyrite through reaction (1). Considering, for unoxidized tailings, an average sulfide content of about 50 wt% (SIWIK et al., 1987) and a carbonate content of 1.5 wt%, and assuming a constant tailings porosity, the length of flow path required to neutralize the H^+ generated from a 1 m thickness of tailings can be calculated. This calculation shows that approximately 25 m of flow path through the tailings is required to neutralize the acid generated from complete oxidation of the sulfides in 1 m of tailings. In the central portion of the impoundment where the water table is shallow and the flow path is long, neutralization of the H^+ generated in the vadose zone may occur, but on the benches of the impoundment where the water table is deep and the flow path is short, low-pH pore waters will probably discharge directly to surface water bodies. This suggests the extensive vadose zone near the tailings margins has important implications with respect to the design of tailings decommissioning programs and future tailings impoundments.

Secondary solid phases precipitated in the vadose zone include gypsum, jarosite, and ferric oxyhydroxides. At several locations, precipitation of jarosite has been extensive enough to cement the tailings into cohesive layers. As sulfide oxidation continues, the thickness and lateral extent of these layers will probably increase. Because of their low gas diffusivities and accreting nature, these layers may limit the entrance of gas-phase O_2 into the tailings, which in turn may lead to a decrease in the rate of sulfide-mineral oxidation below this layer.

As the zone of low-pH conditions becomes more extensive, Fe^{3+}, which is more mobile under low-pH conditions, will become an increasingly important oxidant. Ferric iron displaced downwards may oxidize sulfide minerals below the depth of gas-phase oxygen penetration, which will tend to increase the Fe^{2+} concentration and may lead to the formation of Fe^{2+}-bearing secondary solids such as melanterite, siderite, and mixed ferrous-ferric hydroxides. These solid phases may limit the concentration of Fe^{2+} and may decrease the concentrations of other metals that are coprecipitated in Fe-rich phases.

The mobility of Co, Cr, Cu, Pb, Mn, Ni and Zn will probably follow patterns similar to those observed in supergene enrichment processes. Pb and Cu will probably remain relatively immobile, and be retained in the impoundment through anglesite precipitation and covellite replacement of sulfide grains. Co, Cr, Mn, Ni and Zn probably will be more mobile and may be extensively removed from the oxidation zone, and possibly from the impoundment, by infiltrating recharge waters.

CONCLUSIONS

Sulfide oxidation is occurring in the vadose zone of the Waite Amulet tailings impoundment. The extent of sulfide oxidation and the measured O_2 gas profiles can be described well by the approximate analytical solution of DAVIS and RITCHIE (1986). Sulfide oxidation has generated low-pH conditions and high concentrations of SO_4^{2-}, Fe^{2+} and other metals. The principal sulfide-oxidation products, H^+, Fe^{2+} and SO_4^{2-}, are being displaced down through the vadose zone of the tailings by infiltrating precipitation. The rate of downward movement of the low-pH conditions is retarded relative to the movement of Fe^{2+} and SO_4^{2-} by H^+-consuming reactions, principally carbonate and aluminosilicate dissolution. Of the secondary mineral phases precipitated in the vadose zone, the most significant are goethite, lepidocrocite, ferrihydrite, jarosite and gypsum; these minerals provide effective solid-phase controls on concentrations of the major ions, Fe^{2+}, SO_4^{2-}, Ca, Na, K, in the tailings pore water.

The concentrations of Co, Cr, Cu, Mn, Pb, Zn, Ni appear to be controlled by processes that are analogous to those recognized in zones of supergene enrichment of weathered sulfide orebodies. Lead concentration seems to be limited by anglesite solubility constraints, and that of Cu limited by covellite formation below the zone of active oxidation. As no discrete secondary Co, Cr, Mn, Ni or Zn solid phases have been identified, the pore-water concentrations of these metals are inferred to be controlled by adsorption or coprecipitation reactions.

Calculations based on the observed oxidation profiles and field measured parameters suggest that, in the absence of an effective remedial program, sulfide oxidation in the vadose zone will continue for several centuries. Discharge of high-Fe^{2+} waters will continue to require treatment for several centuries beyond that time. Coincidently, the low-pH zone will expand and the displacement of metals down through the impoundment and into the adjoining surface water environment will increase.

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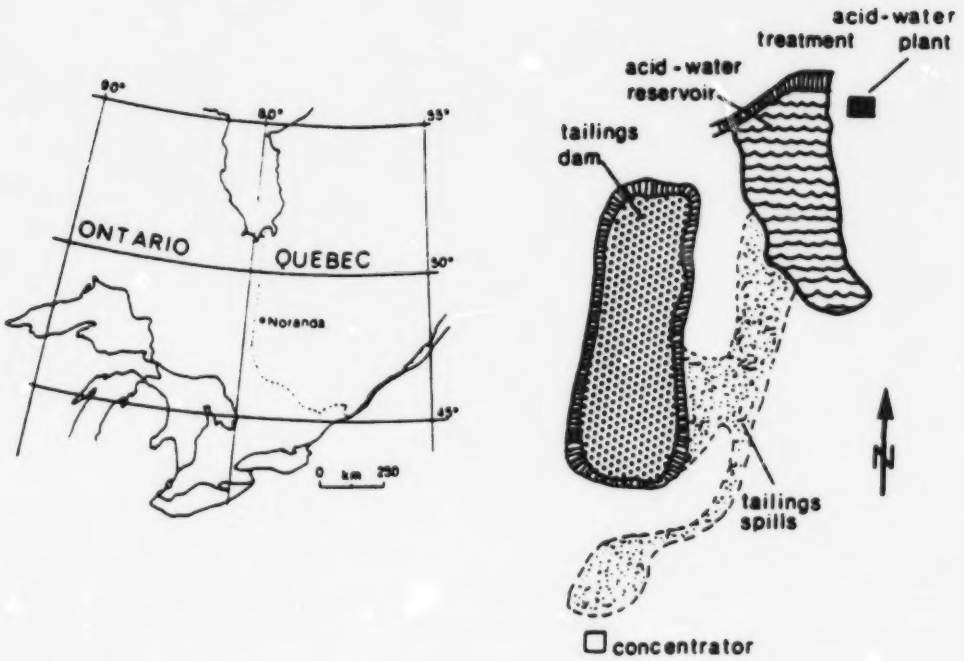

Figure 1. Location of the Waite Amulet study area and general plan of the tailings site.

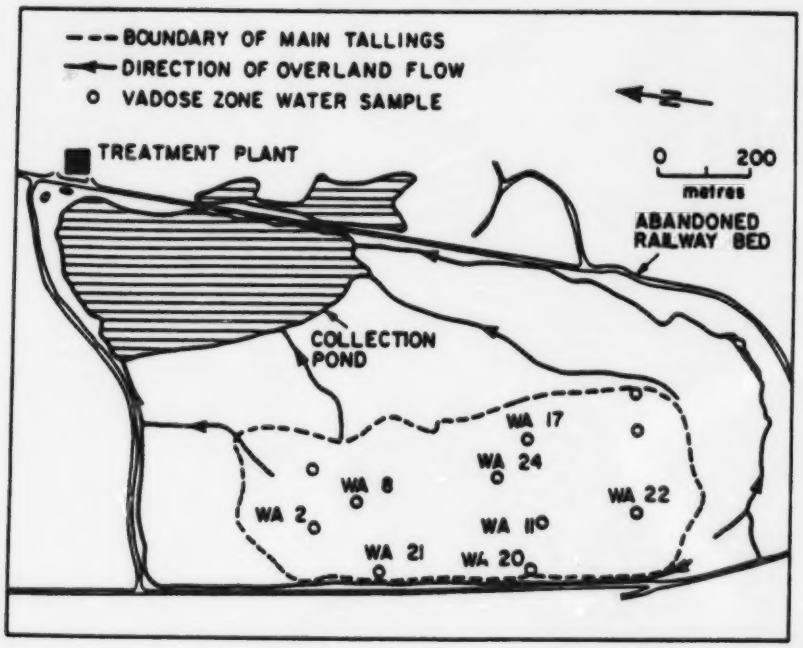

Figure 2. Plan view of the Waite Amulet tailings impoundment and the local drainage system. Cored boreholes are shown by open circles.

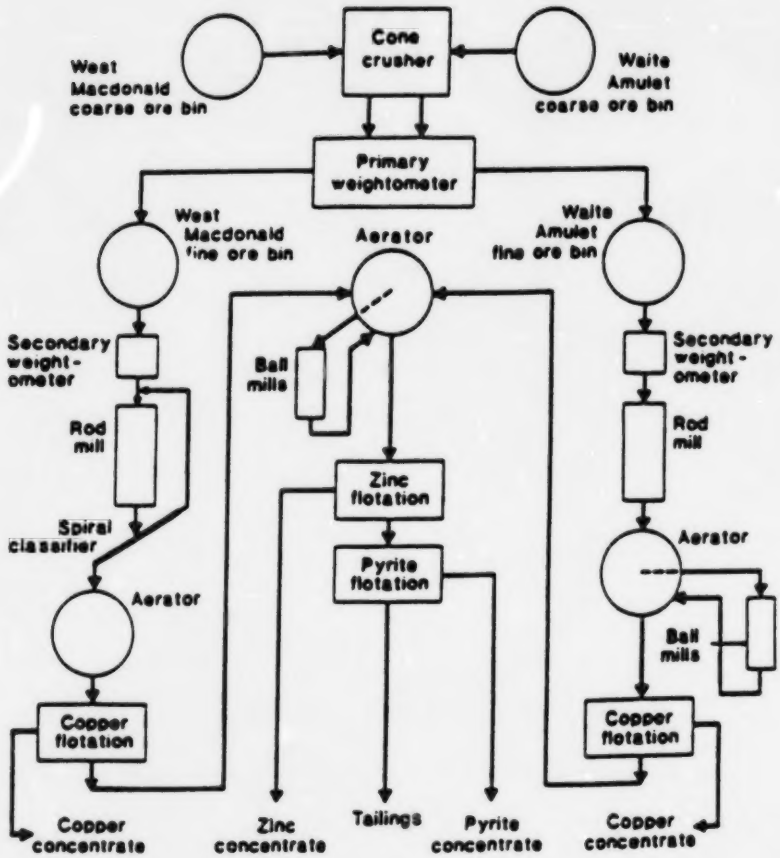

Figure 3. Flowsheet of the milling process at the Waite Amulet mill (from Palmer, 1957 and Siwik, 1986).

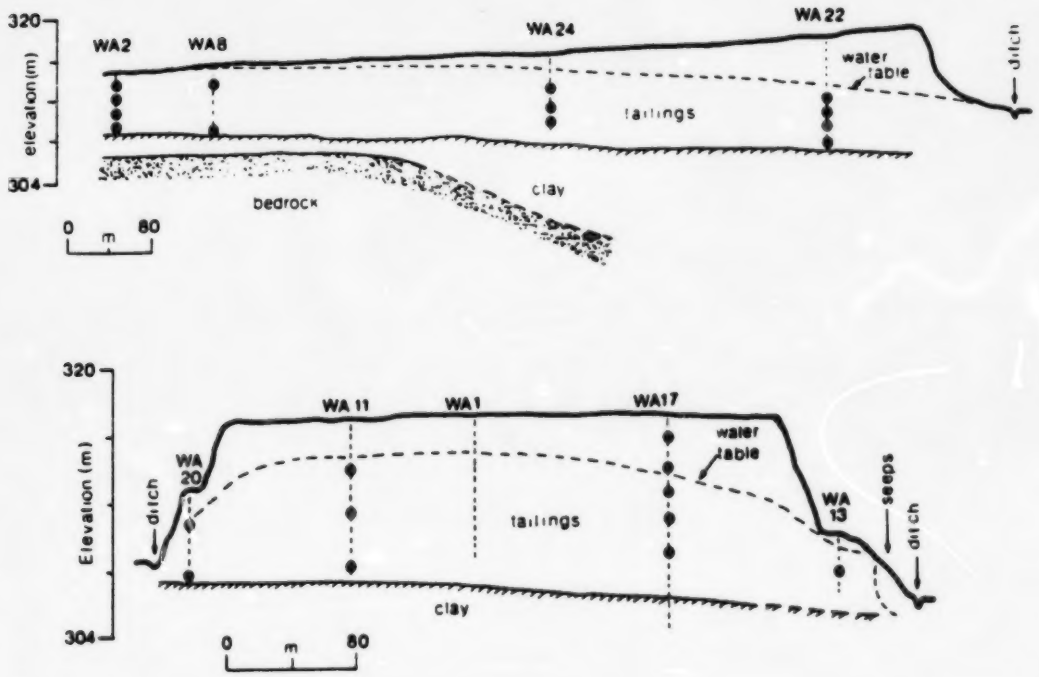

Figure 4. Longitudinal (top) and transverse (bottom) profiles through the Waite Amulet tailings impoundment. Dots at drill sites represent piezometer locations.

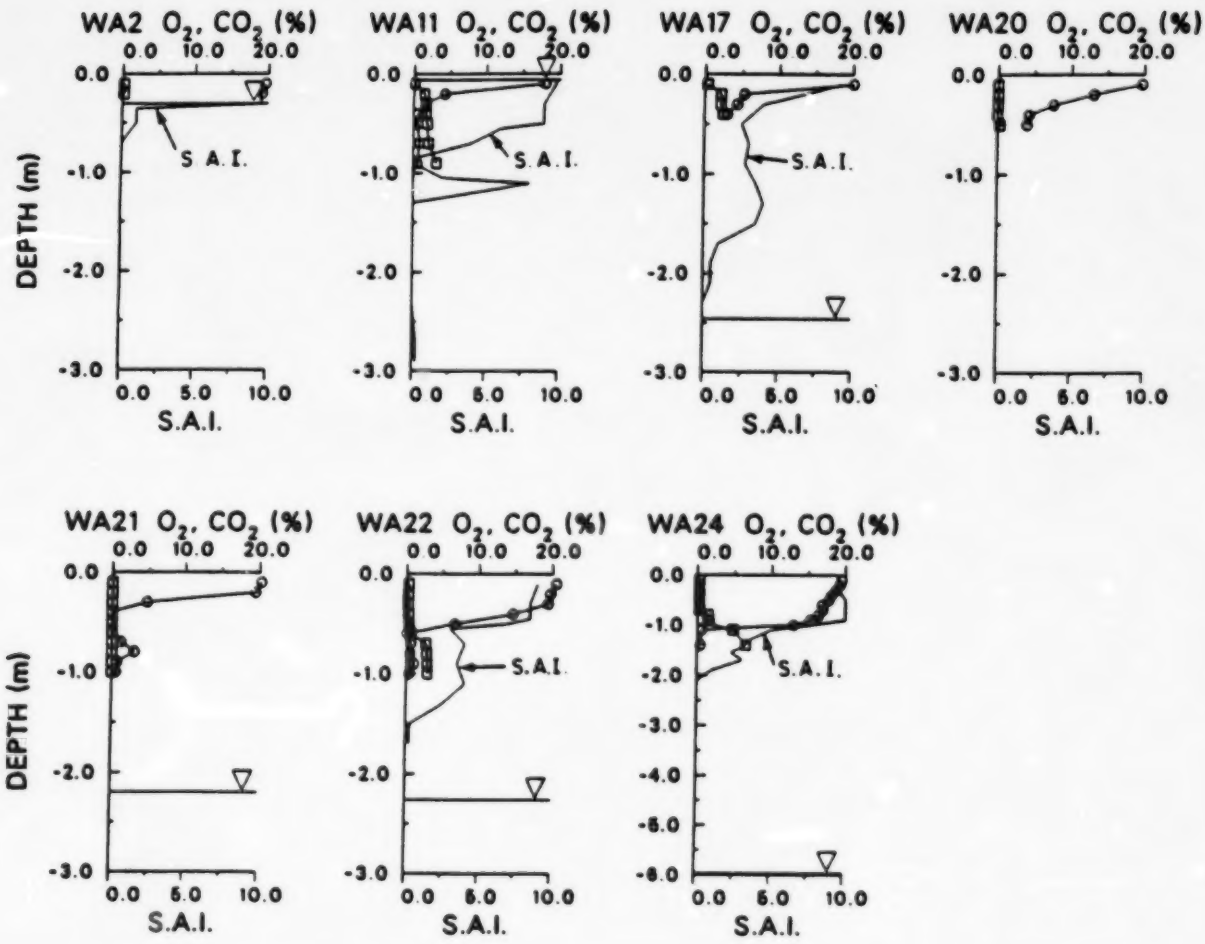

Figure 5. Oxygen (circles) and carbon dioxide concentrations and sulfide alteration index (S.A.I.) (no markers) versus depth. Sulfide alteration index not available for WA20 and WA21.

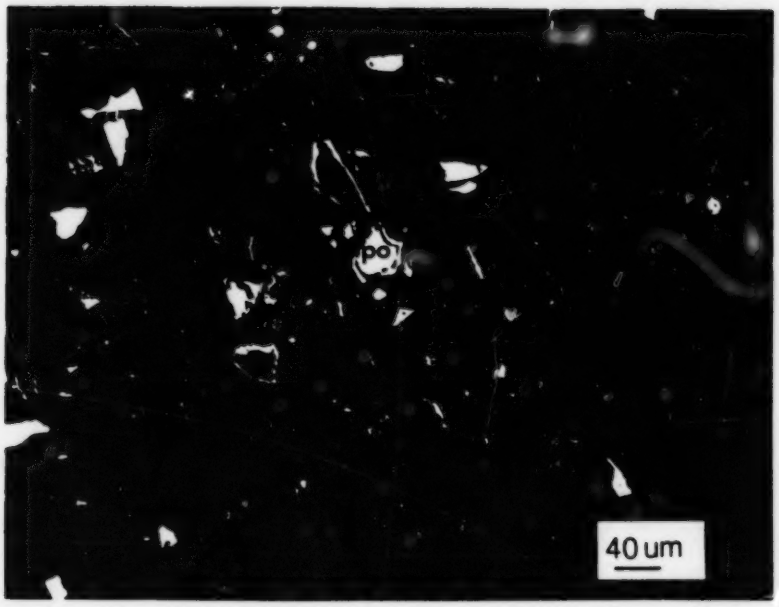

Figure 6. Pyrrhotite (po) core rimmed by marcasite. Several grains have only minute residuals of pyrrhotite at the core, and other grains have a whitish rim of marcasite surrounding a black core of iron sulfates, the combination representing an atoll-texture pseudomorphism of pyrrhotite. Magnetite (m, medium grey) has not been affected to any extent. Reflected light, air; sample WA20-5B.

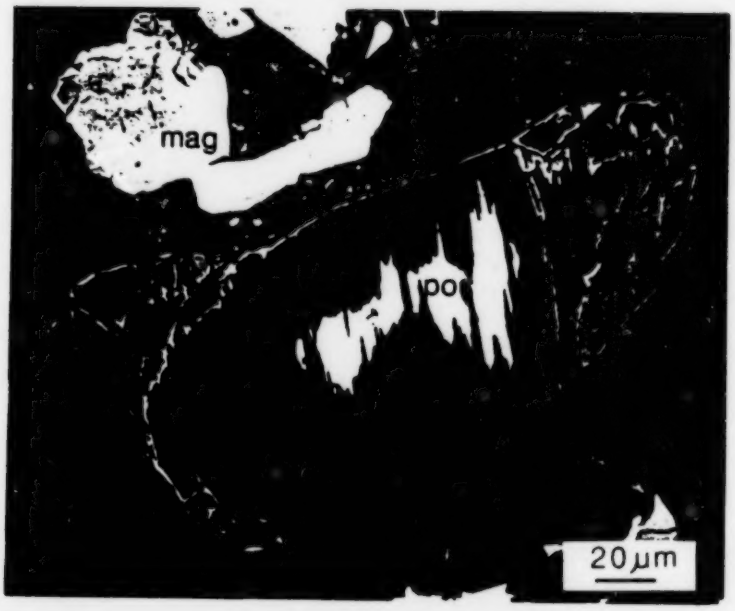

Figure 7. Backscattered-electron micrograph showing a large former pyrrhotite grain in which only residuals of the sulfide (po) remain after replacement by iron sulfate (sf). The irregular, whiter peripheral veinlets and rim are enriched in iron and probably are goethite. Adjacent magnetite grain (mag) is relatively unaltered. Sample WA20-9.

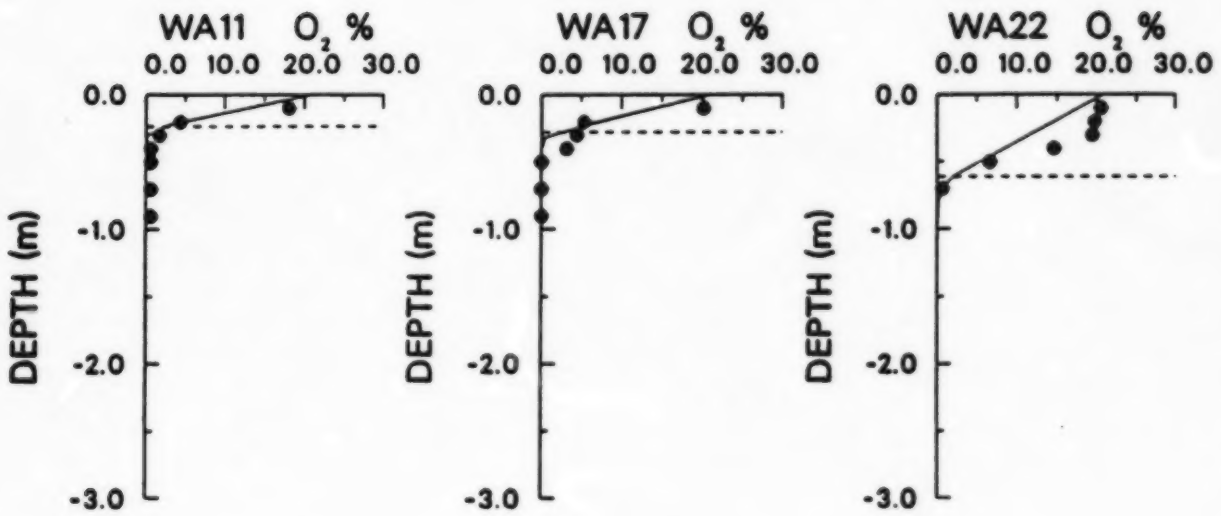

Figure 8. Oxygen concentrations versus depth at locations WA11, WA17 and WA22 showing calculated (smooth curve) and measured (filled circles) O_2 concentrations.

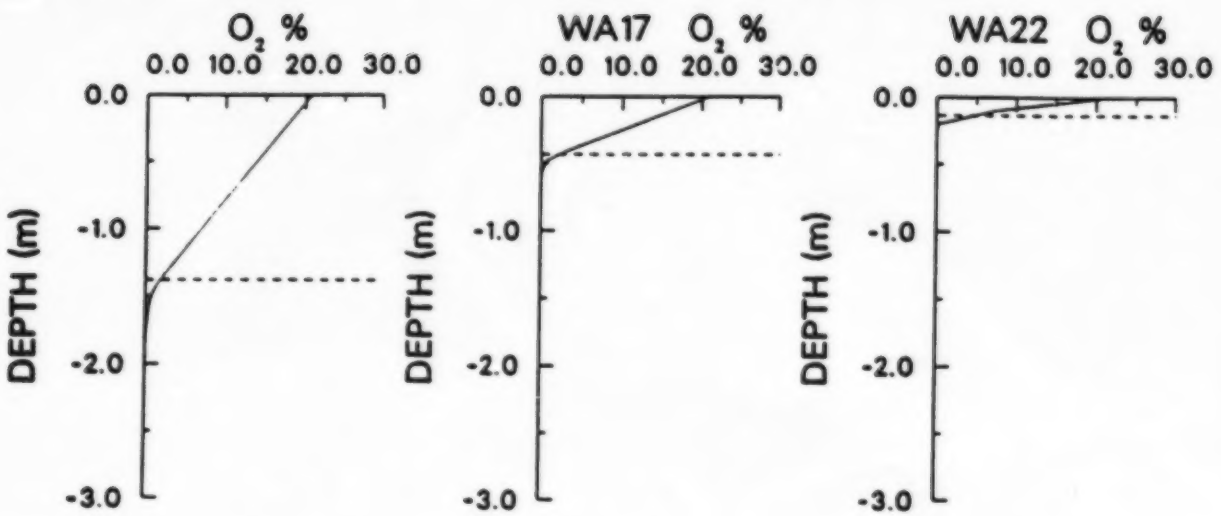

Figure 9. Calculated oxygen concentration versus depth using oxygen diffusivities (D_1) of 1 x 10^{-5}, 1 x 10^{-6} and 1 x 10^{-7}, respectively.

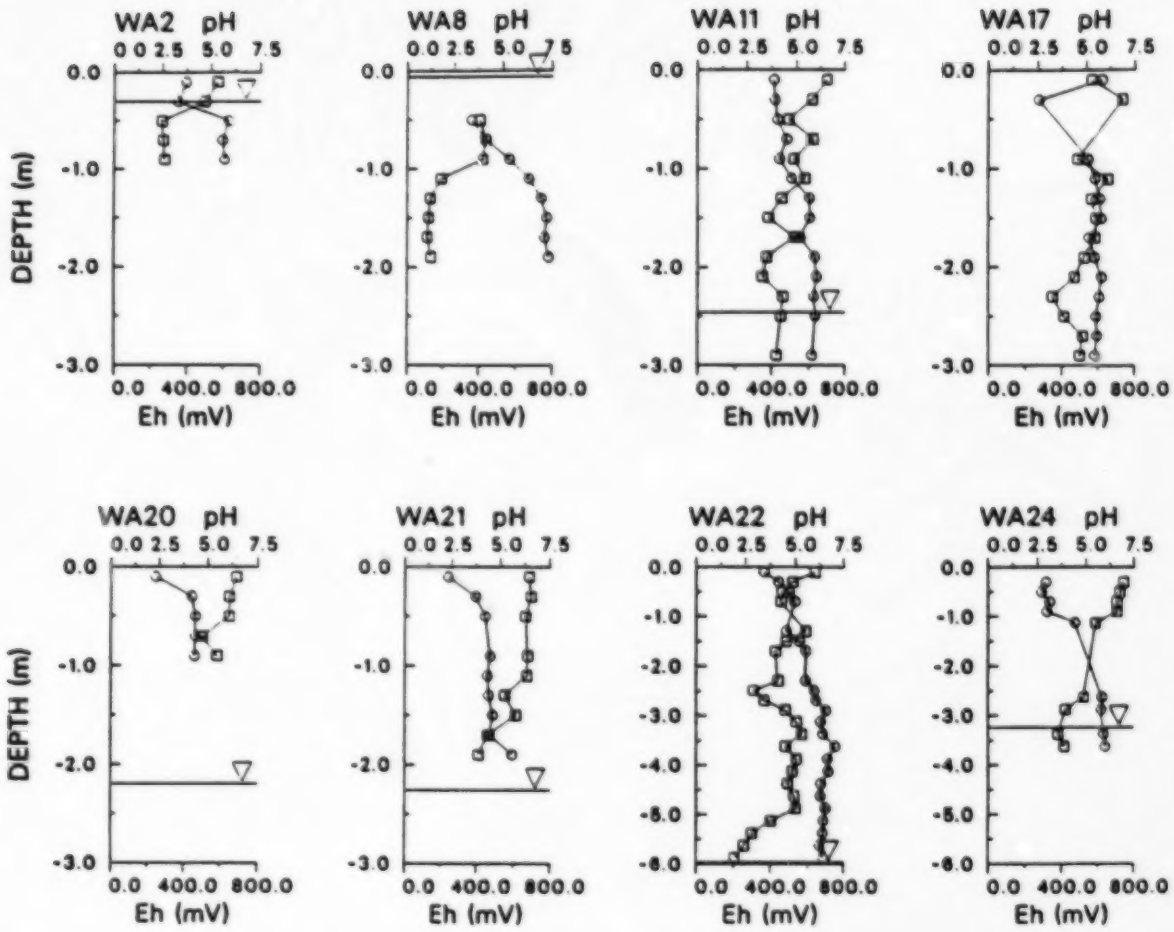

Figure 10a. Profiles of pore-water chemistry versus depth, showing pH (circles) and Eh (squares).

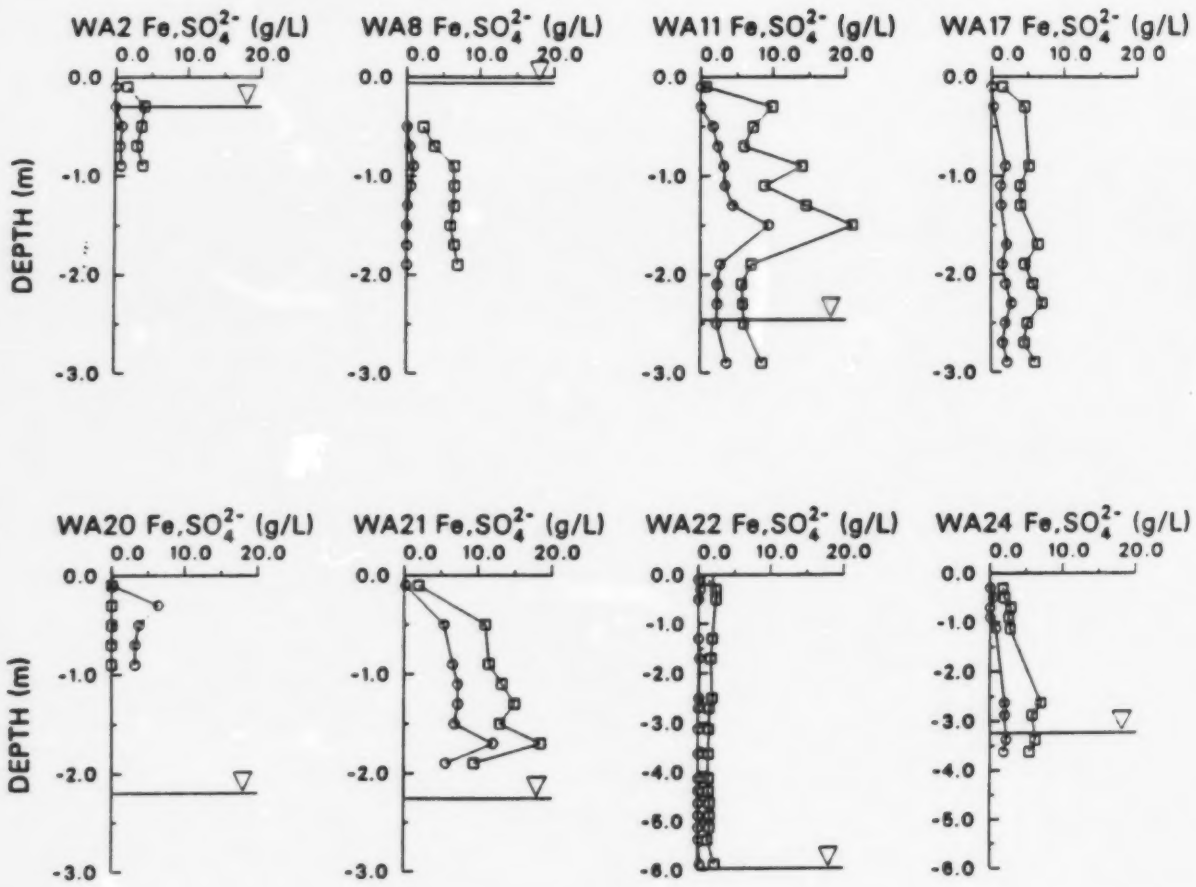

Figure 10b. Profiles of pore water chemistry versus depth, showing Fe (circles) and SO_4^{2-} (squares).

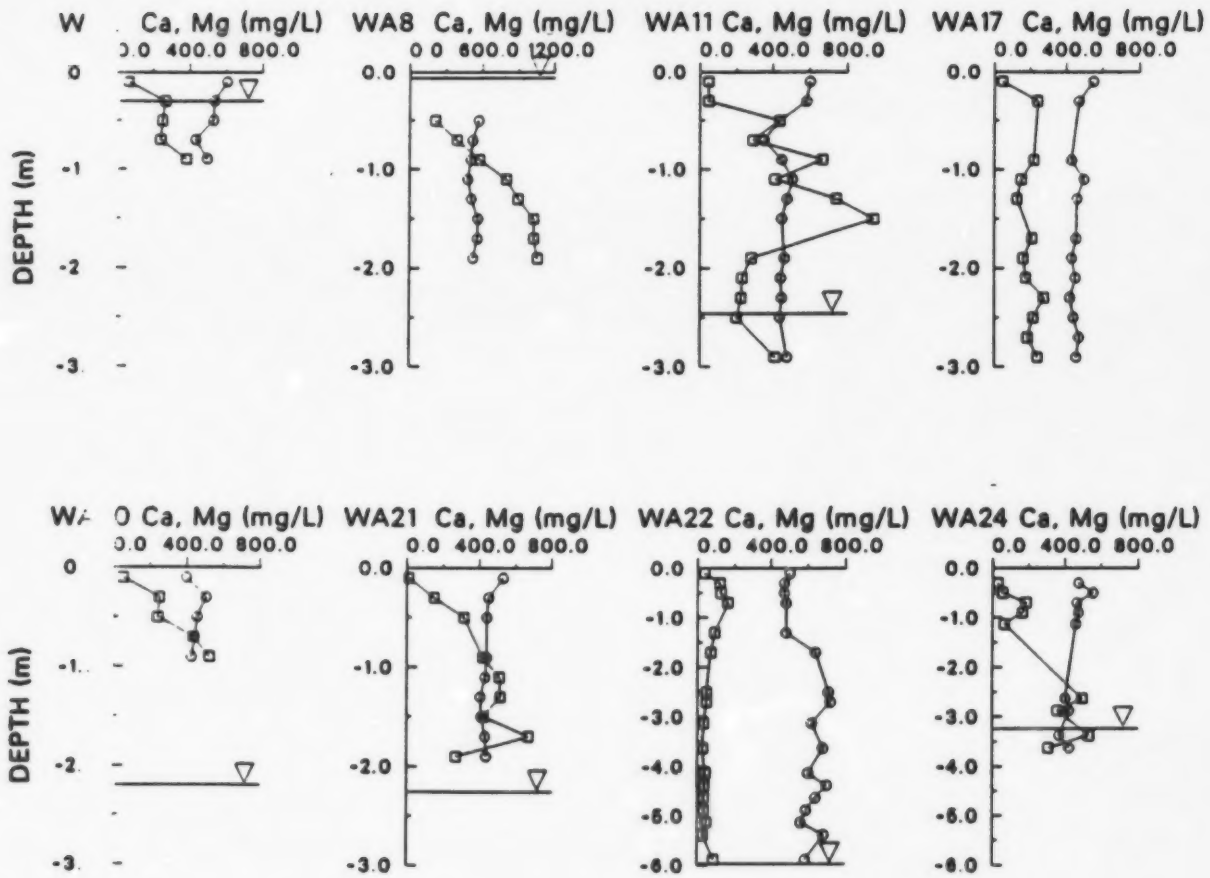

Figure 10c. Profiles of pore water chemistry versus depth, showing Ca (circles) and Mg (squares).

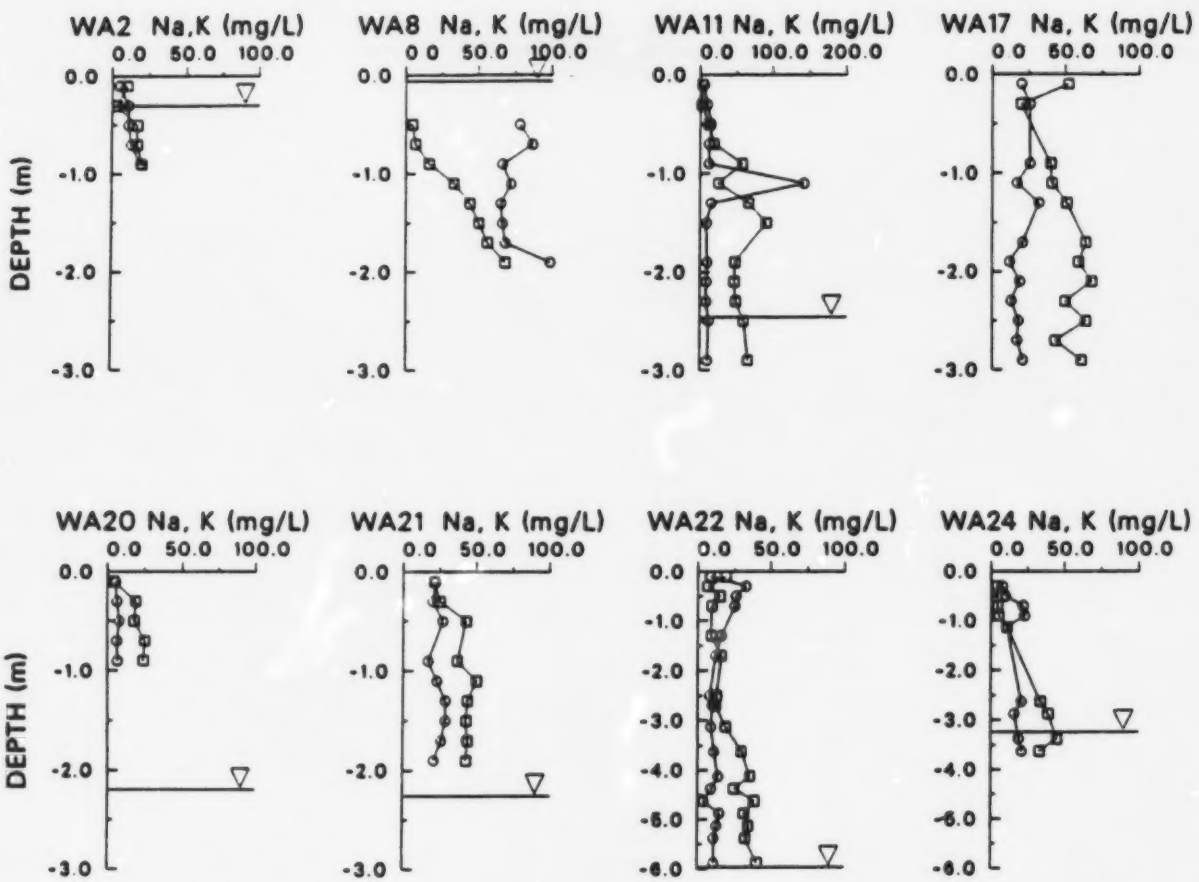

Figure 10d. Profiles of pore water chemistry versus depth, showing Na (circles) and K (squares).

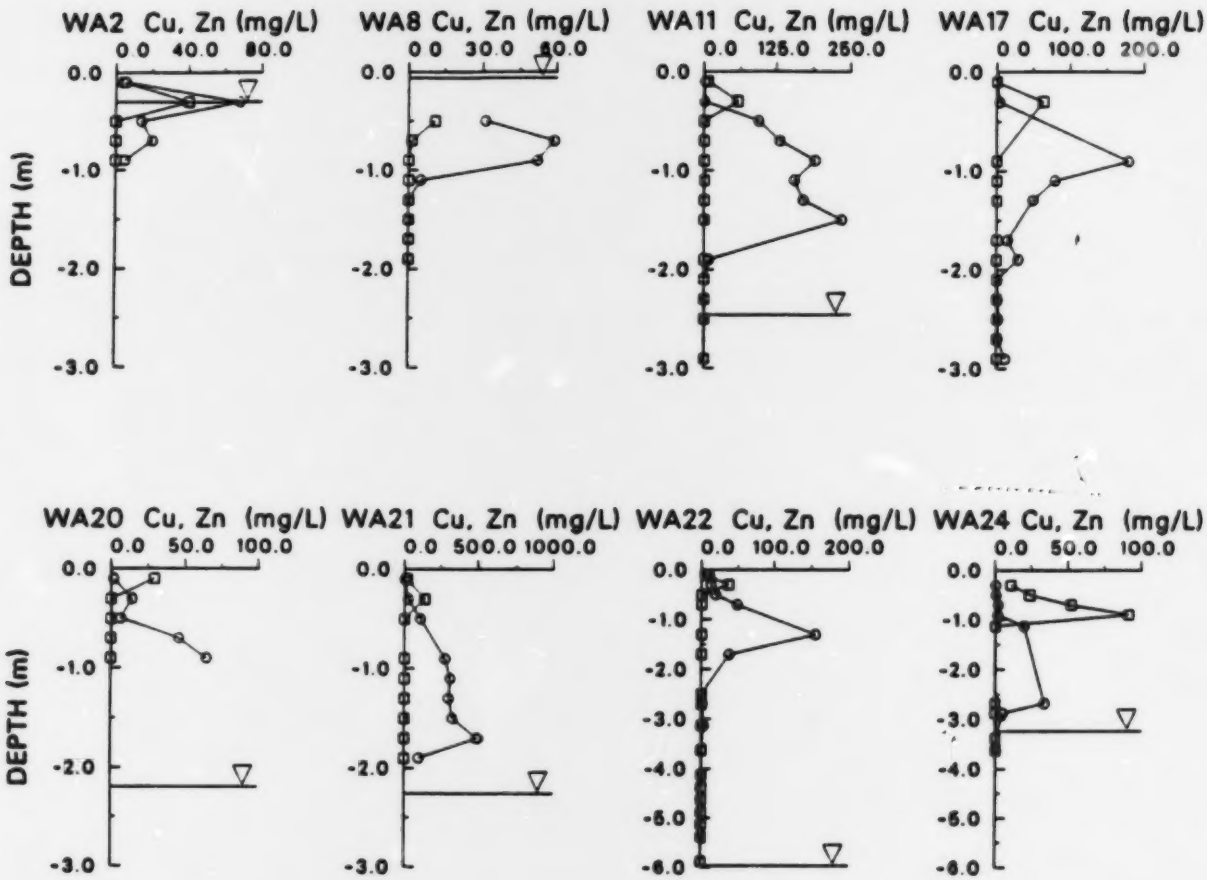

Figure 10e. Profiles of pore water chemistry versus depth, showing Zn (circles) and Cu (squares).

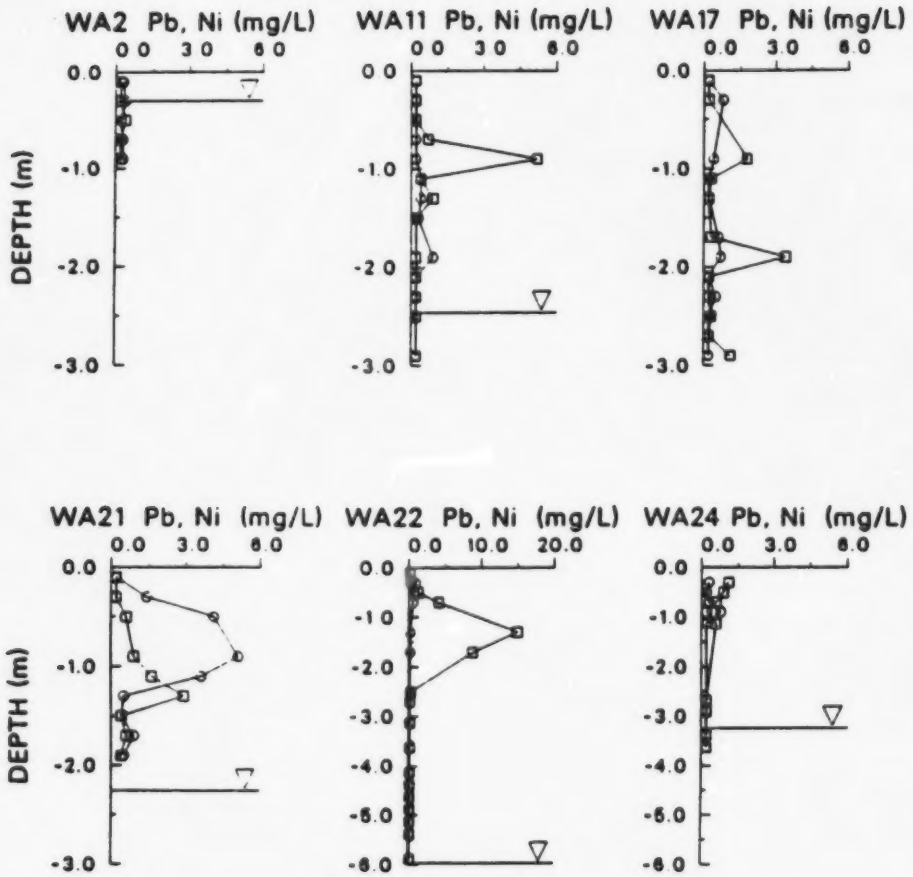

Figure 10f. Profiles of pore water chemistry versus depth, showing Pb (circles) and Ni (squares).

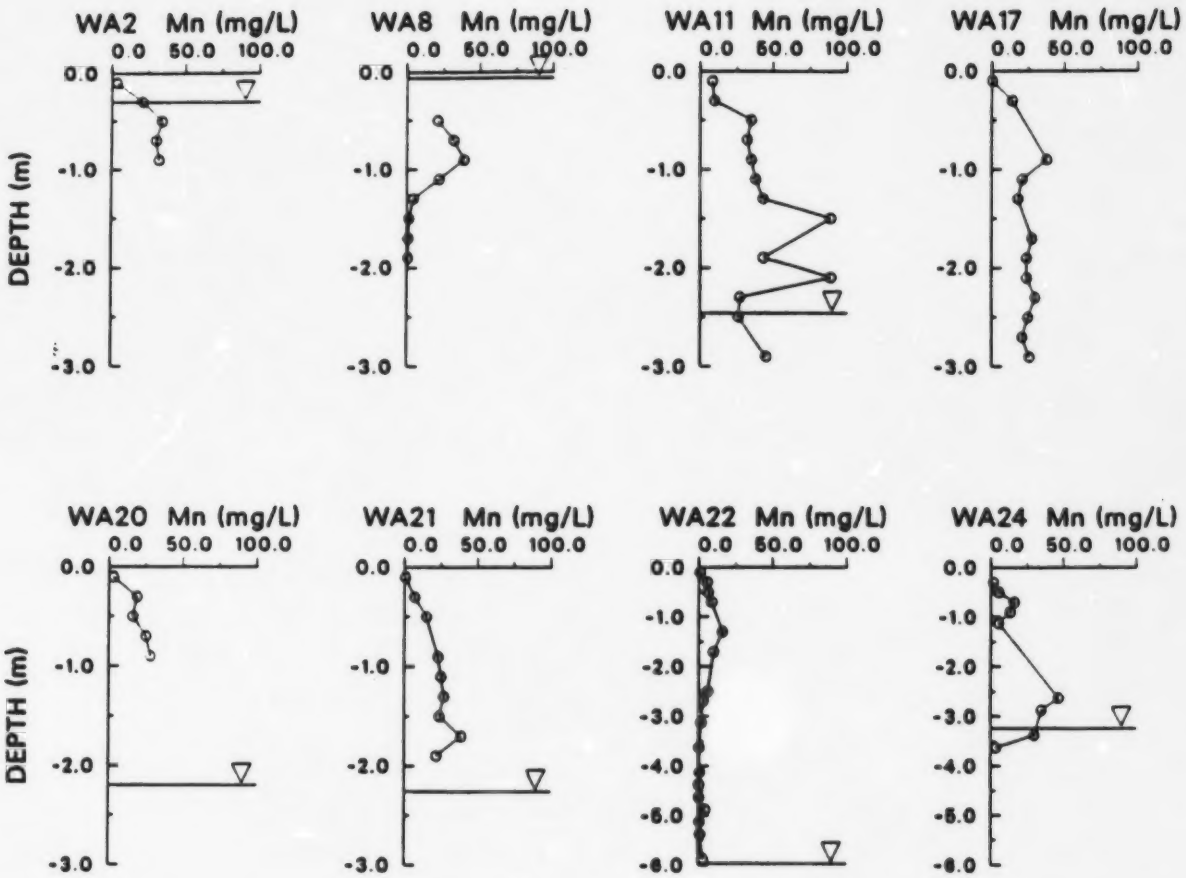

Figure 10g. Profiles of pore water chemistry versus depth, showing Mn.

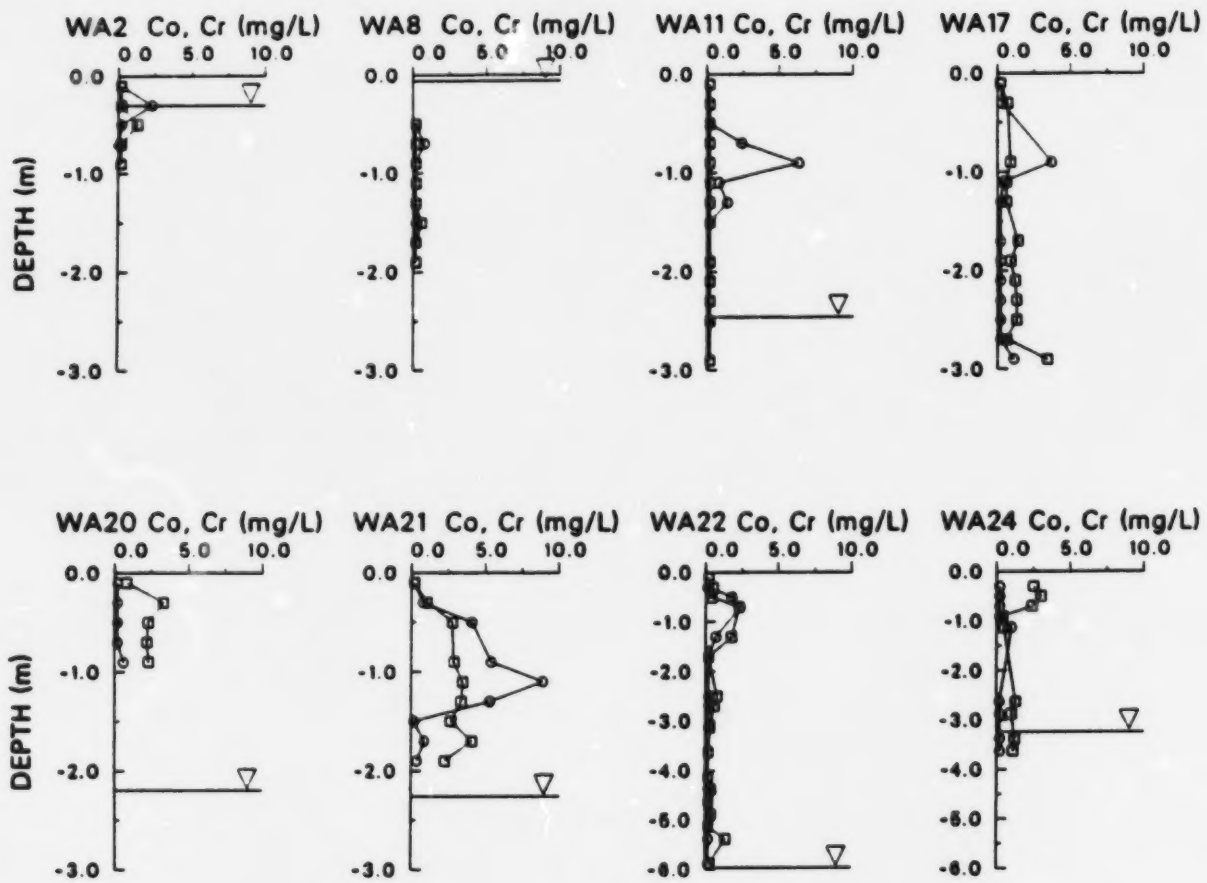

Figure 10h. Profiles of pore water chemistry versus depth, showing Cr (circles) and Co (squares).

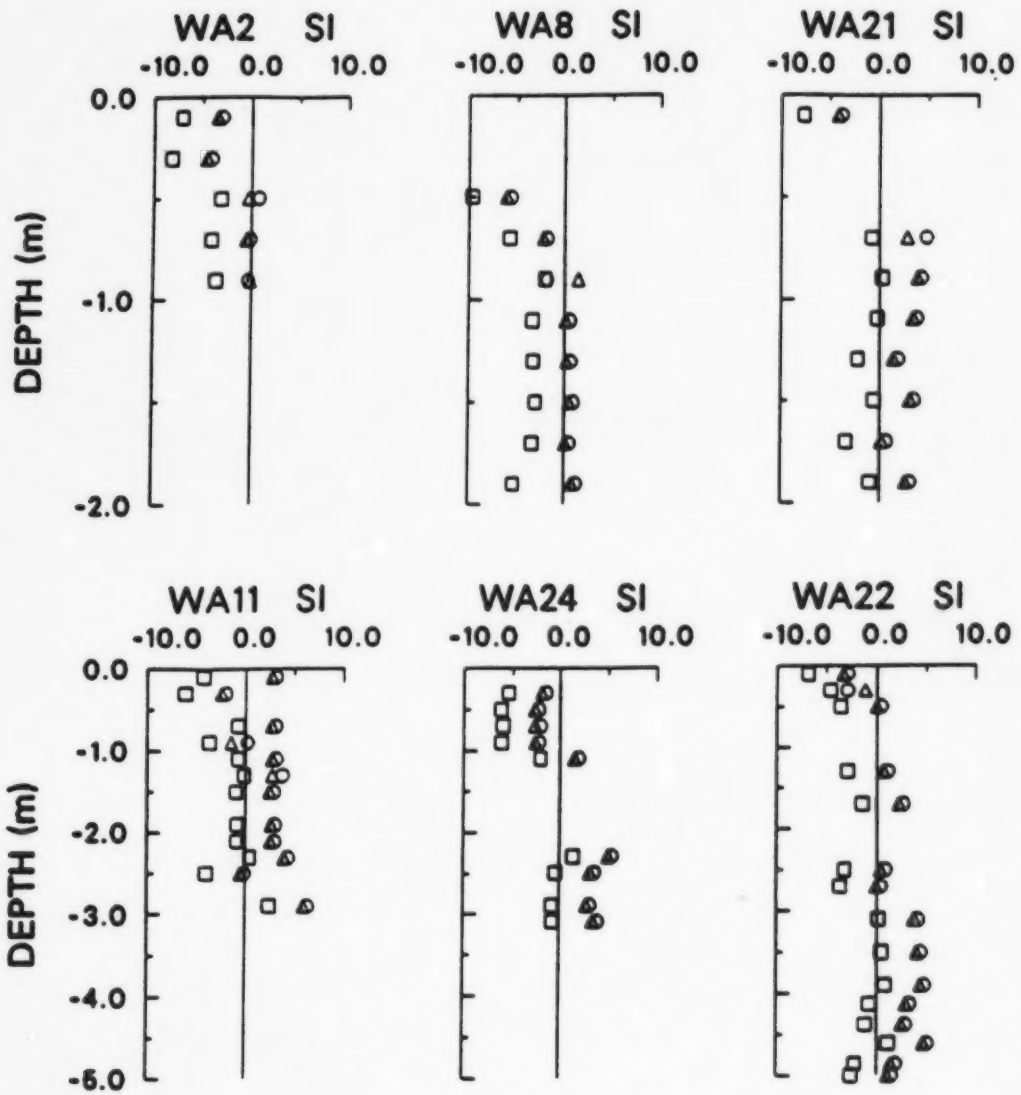

Figure 11. Profiles of saturation index (SI) versus depth for the ferric oxyhydroxide minerals $Fe(OH)_3$ (squares), goethite (circles) and lepidocrocite (triangles).

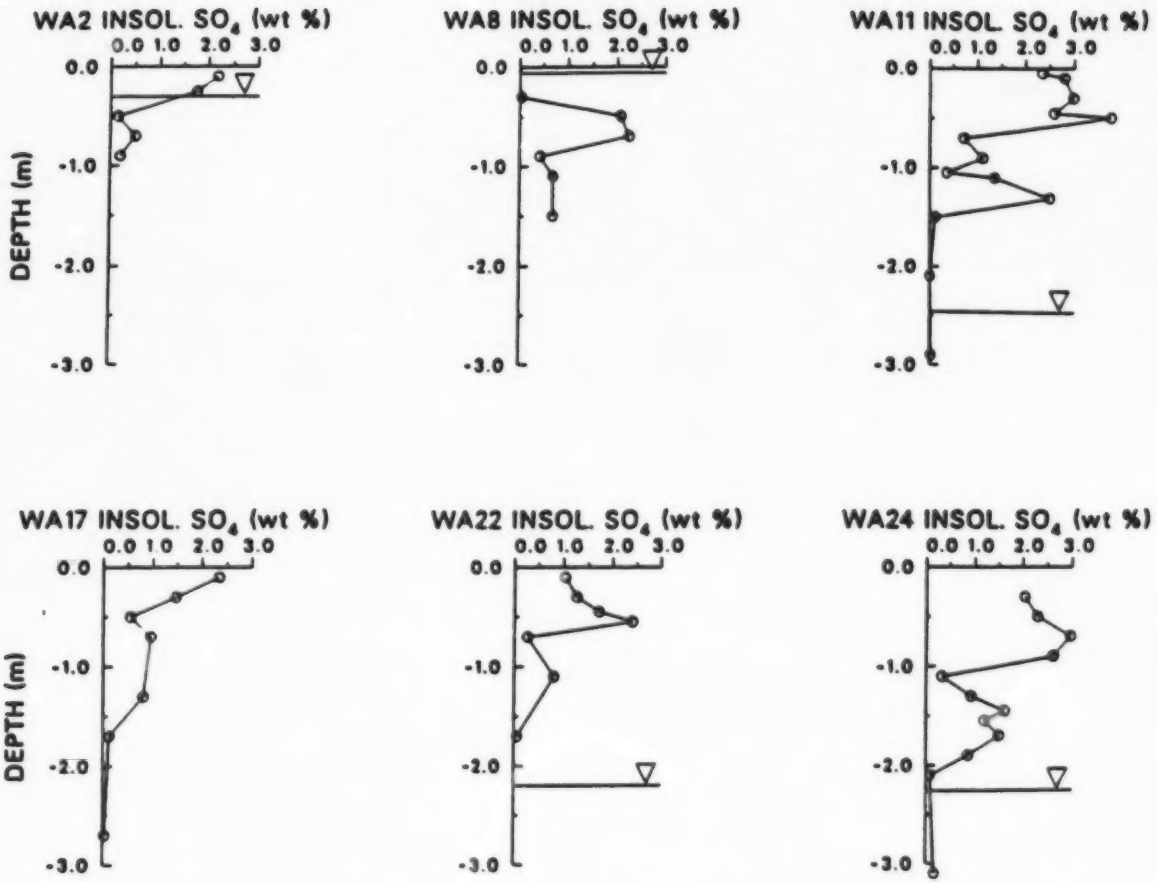

Figure 12. Variations in "insoluble" sulfate contents, interpreted as sulfate contained in secondary jarosite.

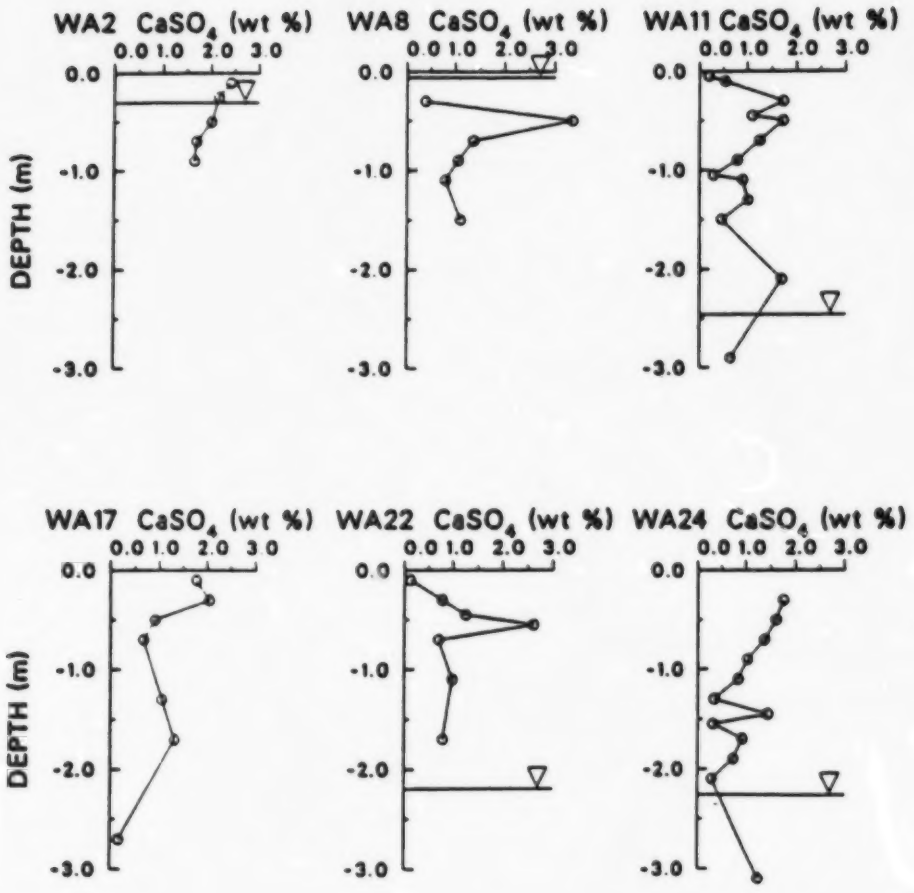

Figure 13. Variations in the gypsum content of the tailings as calculated on the basis of the Ca content of the water-soluble fraction of the tailings solids.

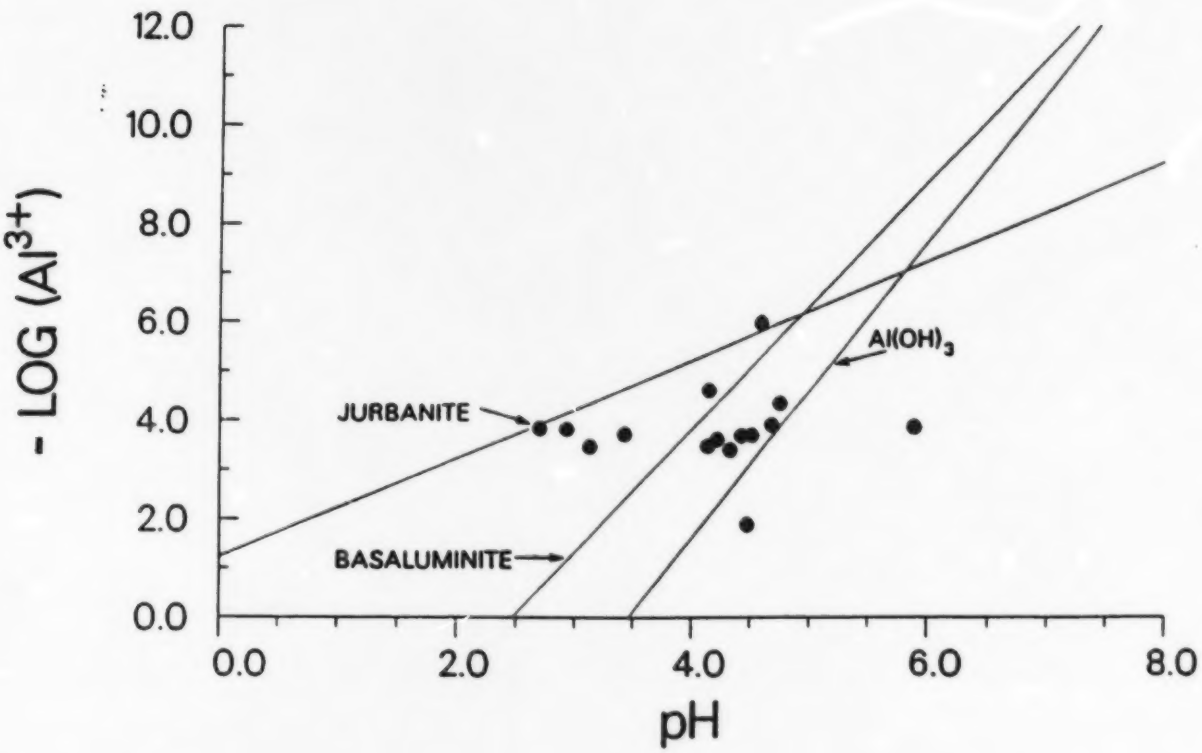

Figure 14. Aluminum activity diagram showing the calculated aluminum activity, plotted versus the measured pH, and lines of equilibria with respect to the aluminum solid phases jurbanite, basaluminite, and amorphous aluminum hydroxide. The lines are plotted for the average sulfate activity of the tailings waters.

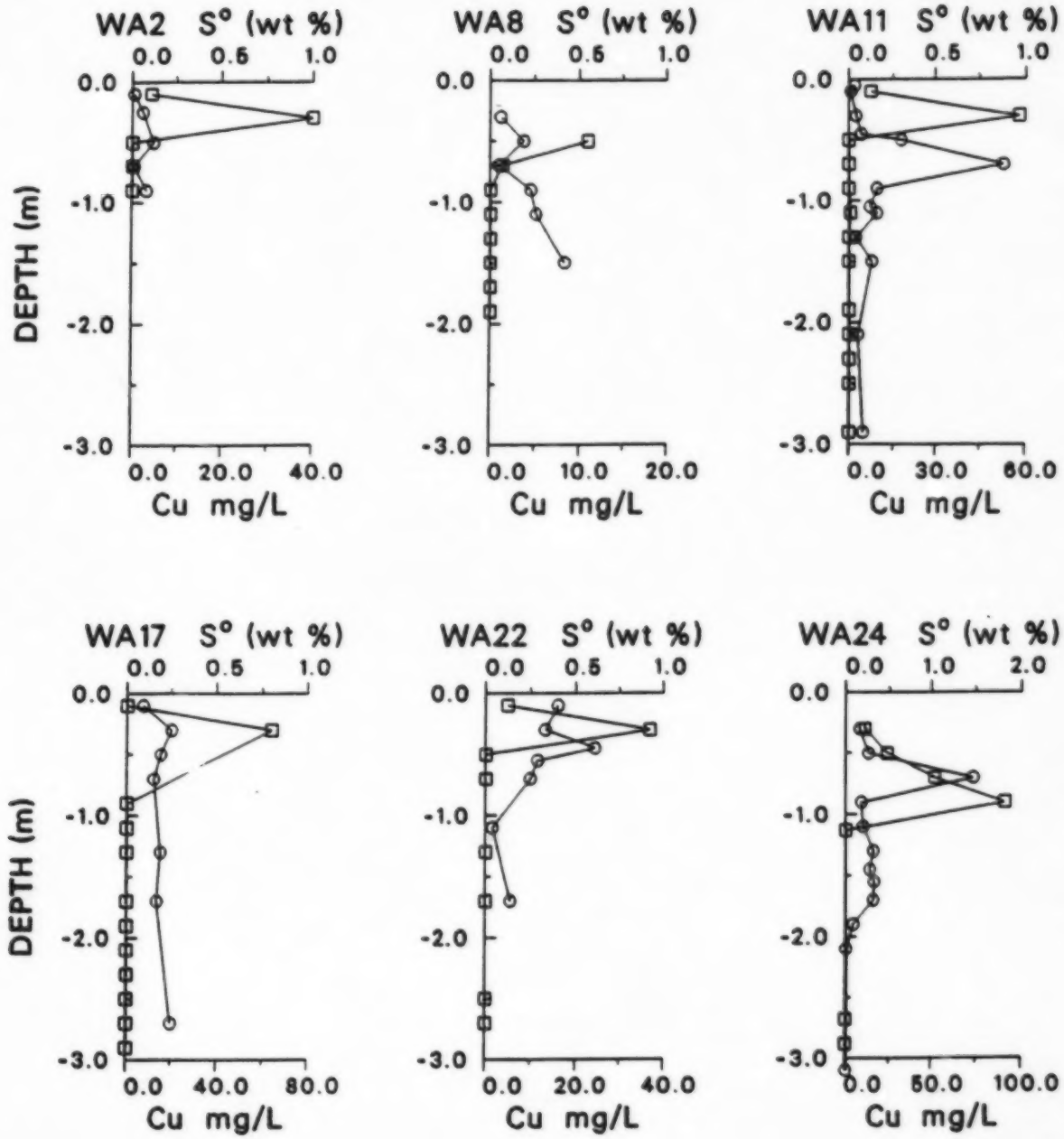

Figure 15. Variations in the elemental sulfur content (circles) of the tailings solids and in the concentrations of dissolved Cu (squares) versus depth.

Table 1. Typical metallurgy and reagents used in processing ores in the Waite Amulet Mill (after PALMER, 1957 and SIWIK, 1986).

METALLURGY	Cu %	Zn %	S %	Au oz/ton	Ag oz/ton
Waite Amulet ore	3.89	3.95	18.91	0.041	8.93
Recoveries (%)	94.49			65.41	65.33
West Macdonald ore	0.13	2.41	46.47	0.027	0.82
Recoveries (%)	7.62			7.53	6.47
Combined zinc recovery (%)		85.6			
Pyrite recovery (%)			83.2		
Pyrite tailings	0.16	0.26	12.82		

REAGENTS	Waite Amulet Cu Flotation	West Macdonald Cu-Ag-Au Flotation	Zinc Flotation	Pyrite Flotation
Sodium sulfide (lb/ton)	1.086	0.302		
NaCN	0.028	0.007	1.870	
Soda Ash	2.336	1.650		
Aerofloat 242	0.066	0.013		
Z-5	0.074			
Frother 73	0.073	0.012	0.065	0.017
Aerofloat 208		0.005	0.093	
$Ca(OH)_2$			0.329	
$CuSO_4$			1.437	
$(NH_4)_2SO_4$			0.185	
Aerofloat 343				0.162

Table 2. Description of the sulfide alteration index as used in the mineralogic study.

NUMERICAL SCALE	DEGREE OF ALTERATION OF SULFIDES
10	pyrrhotite and pyrite obliterated; only traces of sulfide, typically chalcopyrite, are present
9	similar to 10, but with few scattered remnant grains of pyrite
8-7	first appearance of trace amounts of pyrrhotite (at scale 8), at scale 7 the vestiges of strongly altered pyrrhotite increase in abundance or degree of preservation
6-2	at scale 6 the pyrrhotite grains have broad alteration rims, but the cores of numerous grains are preserved, gradation to scale 2 is marked by the appearance of narrower alteration rims and a predominance of unaltered grains.
1-0	only a few grains of pyrrhotite are weakly altered along rims and fractures; 95% of grains have sharp, fresh margins.

Table 3: Constant parameters used in the model of DAVIS and RITCHIE (1986)

PARAMETER	VALUE	SOURCE
D_2	2.6×10^{-10} m^2 s^{-1}	2
U_o	0.265 kg m^{-3}	1
L	10 m	2
A	0.0002 m	2
ϵ	1.746	1
ρ_s	1.0×10^{-2} kg m^{-3}	3
γ	0.03	1

1. From DAVIS and RITCHIE (1986)
2. Estimation
3. Measured

Table 4: Variable parameters used in the model of DAVIS and RITCHIE (1986) and calculated model results.

PIEZOMETER NEST	WA-11	WA-17	WA-22
p (porosity)	0.50	0.58	0.52
D_1 ($m^2\ s^{-1}$) (Reardon and Moddle)	1.7×10^{-7}	5.9×10^{-7}	8.0×10^{-7}
D_1 ($m^2\ s^{-1}$) (Millington and Shearer)	6.0×10^{-8}	1.4×10^{-7}	3.3×10^{-7}
D_1 ($m^2\ s^{-1}$) (modelled)	3.0×10^{-7}	4.2×10^{-7}	2.0×10^{-8}
t_d (years)	150 - 370	260 - 640	180 - 460